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BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR
Division of Chemical Science

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ACADEMICIAN NIKOLAI DMITRIEVICH ZELINSKII

(Centennial of his birth)

B. A. Kazanskii

Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 2, pp. 193-196, February, 1961

Nikolai Dmitrievich Zelinskii was born on February 6 (Gregorian calendar) 1861, in Tiraspol'. After graduating from the University in Odessa in 1884, Zelinskii worked with Professor I. Wislicenus in Leipzig and with Professor V. Meyer in Göttingen. On his return from abroad, Zelinskii became Privatdozent at the University in Odessa where he defended a master's dissertation on "Isomerism in the thiophene series" (1889) and a doctor's dissertation on "Phenomena of stereoisomerism among saturated organic compounds" (1891).

In 1893 Zelinskii was appointed extraordinary professor of Moscow University and director of the analytical chemistry laboratory and part of the organic chemistry laboratory; the other part of the laboratory remained under the direction of V. V. Markovnikov. From this time until his death in 1953, all Zelinskii's teaching activities were connected with Moscow University, except for the period from 1911 to 1917, when he was forced to work elsewhere, having left the university as a protest against the actions of the Tsarist Minister of National Education Kasso, who abolished the autonomy of the university.

Zelinskii was elected a Corresponding Member of the Academy of Sciences of the Soviet Union in 1926 and a full member in 1929. He was awarded the title of Hero of Socialist Labor in 1945.

In 1935 Zelinskii participated in the organization of the Institute of Organic Chemistry of the Academy of Sciences, USSR, which now bears his name, and until his death he directed a section, consisting of three laboratories. Zelinskii died on August 31, 1953, at the age of 93.

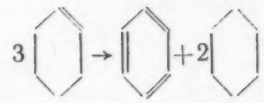
Zelinskii's scientific activity was extensive and varied; its characteristic traits were a progressive approach and a tendency to use scientific achievements for the national economy and public health. Zelinskii was always to the fore in science and had an acute instinct for anything new. In his first dissertation he made a contribution to the chemistry of thiophene, which had been isolated recently by V. Meyer from coal tar. Zelinskii devoted his second dissertation to the stereochemistry of organic compounds, thus expanding this branch of organic chemistry, which at that time was newly established by the work of Pasteur, Le Bel, Van't Hoff, Wislicenus, and others.

In his later years he was interested in the synthesis and conversions of hydrocarbons and catalytic reactions of organic compounds. Zelinskii was first interested mainly in alicyclic hydrocarbons, as the most characteristic components of petroleums from all of the deposits known at that time, and with his students he synthesized these hydrocarbons in order to use them as synthetic standards for a more thorough study of the composition of petroleum. As was also considered by our other outstanding chemists occupied with problems on the chemistry of petroleum, D. I. Mendeleev and V. V. Markovnikov, Zelinskii believed that a study of the composition of petroleum was extremely important as he foresaw that petroleum hydrocarbons could be a plentiful, varied, and promising starting material for the synthesis of such organic compounds as halogen derivatives, alcohols, aldehydes, ketones, acids, esters, nitro derivatives, many aromatic compounds, etc. Zelinskii described this variety of compounds as "products of the highest chemical value, obtained from petroleum hydrocarbons." Later on, Zelinskii and his students enlarged the scope of their investigations in the field of hydrocarbon chemistry; they synthesized for the first time tens of hydrocarbons of various types and structures, studied their physical and chemical properties, and contributed much toward the development of methods for their isolation from complex natural mixtures and reliable identification.

Special attention was paid to the reactivity of various types of hydrocarbons. The solution of these problems was greatly helped by Zelinskii's investigations in the early 1900s on heterogeneous catalysis, mainly in the presence of metals, namely, platinum, palladium, and nickel, and also in the presence of aluminum chloride. As these investigations developed, they centered at first around the catalytic dehydrogenation of cyclohexane hydrocarbons $C_6H_{12} \rightarrow C_6H_6 + 3H_2$. It was found that in the presence of platinum, palladium, and nickel deposited on alumina, these

hydrocarbons were converted smoothly into the corresponding aromatic hydrocarbons at low temperatures with the elimination of hydrogen and without the formation of by-products. The kinetics of these conversions were studied and this gave valuable data for the theory of heterogeneous catalysis, in particular, for the development of the multiplet theory of catalysis of A. A. Balandin. This reaction made possible a more thorough and detailed study of the qualitative and quantitative composition of ligroins of various petroleums, particularly of USSR petroleums. The presence of six-memebered naphthenes in them was thus established and this made it possible to plan the most advantageous use of such ligroins as fuel and as starting materials for organic synthesis. A series of industrial processes for catalytic aromatization of hydrocarbons was based on this reaction.

The catalytic dehydrogenation of cyclohexane and its homologs is accompanied by another, unusual process, which occurs in the presence of the same catalysts, namely, the disproportionation of hydrogen between several cyclohexane molecules ("irreversible catalysis") to form benzene and cyclohexane:



The kinetics of this reaction were also studied and the role of this process in the dehydrogenation of six-membered naphthenes elucidiated. Zelinskii and his co-workers discovered the catalytic hydrogenolysis of five-membered naphthenes in the presence of platinum to form paraffins of corresponding structure and the role of this reaction in the aromatization of ligroins.

The conversions of paraffin hydrocarbons also interested Zelinskii. Together with his students, he studied the catalytic dehydrogenation of the simplest paraffins in order to synthesize dienes, which are the starting materials in the synthesis of rubber. For several years Zelinskii studied the polymerization of acetylene at high temperatures in the presence of activated charcoal. This original version of the Berthelot reaction made it possible to synthesize a series of simple and complex aromatic hydrocarbons from acetylene.

Zelinskii and his students devoted much attention to the conversions of various types of hydrocarbons in the presence of aluminum halides. They studied cracking with aluminum chloride and isomerization of hydrocarbons rings (five-, six-, seven-, and eight-membered rings). Isomerization in the presence of other catalysts and, in particular, the migration of double bonds of olefins were also studied. All these reactions connected various types of hydrocarbons by a series of direct conversions from one to another and facilitated their interconversions and practical use.

Zelinskii repeatedly put forward ideas on the role of catalysts in heterogeneous catalytic reactions; he considered that the catalyst facilitated a change in the form of the reacting molecules, leading to their specific conversions and accelerating the latter. Other catalytic reactions of organic compounds also attracted his attention. Thus, he was interested in the synthesis of hydrocarbons from carbon monoxide and hydrogen and put forward a series of original hypotheses on the mechanism of this reaction.

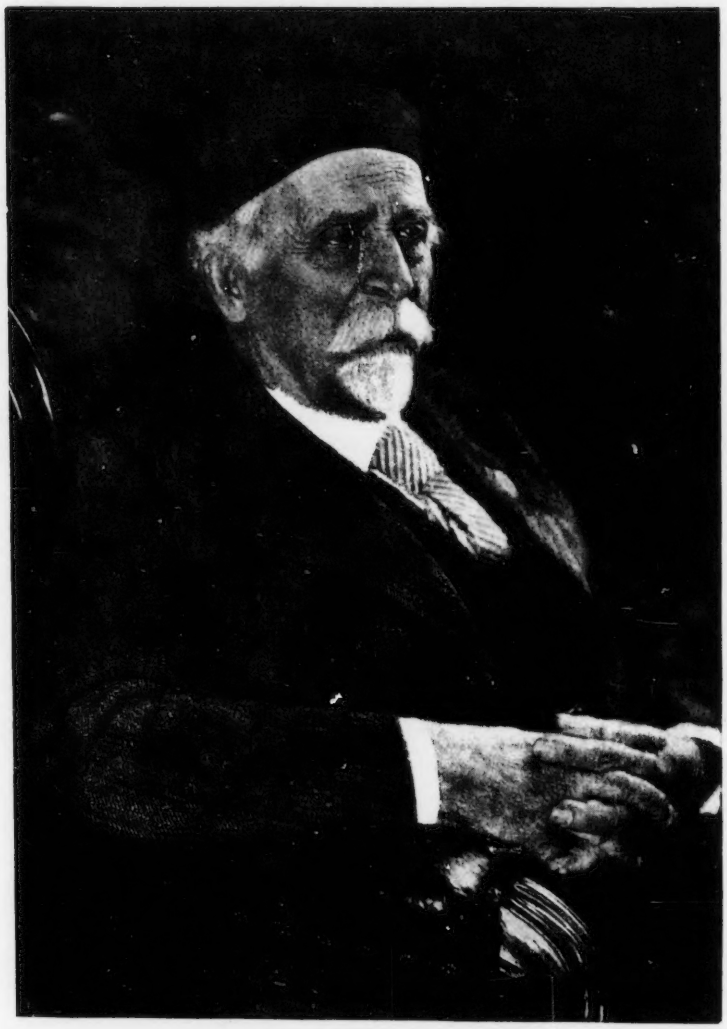
As Zelinskii wished to prepare other types of more reactive compounds from petroleum hydrocarbons, he synthesized ketones by treating naphthenes and paraffins with organic acid chlorides in the presence of aluminum chloride. Catalytic conversions of heterocycles also attracted his attention. The hydrogenation of pyrrole and pyridine, dehydrogenation of pyrrolidine, hydrothiophene, and catalytic desulfurization of sulfur-containing ligroins were all problems which actively interested Zelinskii and he returned to their investigation repeatedly.

Catalytic conversions of organic compounds and, in particular, of hydrocarbons, were Zelinskii's favorite subject for investigation for a number of decades. However, he was also interested in other, completely different fields of organic chemistry, and in particular, he was interested in substances connected with life processes. It is curious that in this field he also approached the problems from point of view of catalysis. Zelinskii and his co-workers carried out a series of investigations on the hydrolysis of proteins with dilute solutions of acids and bases at high temperatures. An investigation of the hydrolysis products led him to put forward some hypotheses on the structure of proteins.

Zelinskii's willingness as a scientist to undertake practical problems created by historical circumstances, is illustrated by his very active and successful work on producing a charcoal gas mask for protection against poisonous war gases. The results he achieved saved many thousands of soldiers in the Russian and Allied armies during the First World War in 1914-1918.

During his scientific activity, which lasted for almost seventy years, Zelinskii was always surrounded by students and co-workers who cooperated very closely with him with great enthusiasm. What assisted Zelinskii in the creation of one of the largest Russian schools of organic chemistry? The main factor was his unshakeable belief in the might and power of science and its fundamental importance in the development of our country. Zelinskii knew how to infect all those who came into contact with him with this belief; his scientific activity was of fundamental importance and serving his country and science were the only stimuli for him.

The following is a quote from Zelinskii's address to youth: "All my life I have been interested in chemistry and rather than weakening, my interest has become ever greater now. Chemistry has often rewarded me with the great enjoyment of finding previously univestigated mysteries of nature; it gave me the chance to serve people, lighten their labor, and free them from some of their suffering and even occasionally, from death; it helped me to become a person of some value to my country; and it determined the way in which I was able to be of some benefit to the Socialist system and the defense of the Soviet Nation. I am sure that anyone who becomes interested in chemistry will never regret choosing this science as his specialty." These words are remembered by all those who worked with Nikolai Dmitrievich Zelinskii and knew him well.



NIKOLAI DMITRIEVICH ZELINSKII

AN INVESTIGATION OF THE EQUILIBRIUM OF THE TERNARY SYSTEM OF METALLIDES Ni_3Nb–Ni_3Ti–Ni_3Ta

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Original article submitted October 2, 1959

In the chemistry of metals, together with the investigation of diagrams of state it is of great interest to study the equilibrium between metallic compounds [1]. The ternary system between the metallic compounds Ni_3Nb–Ni_3Ti–Ni_3Ta, investigated by the authors, is a part of the quaternary system nickel-niobium-titanium-tantalum, obtained by the cutting of the tetrahedral diagram by a singular ternary component system (Fig. 1).

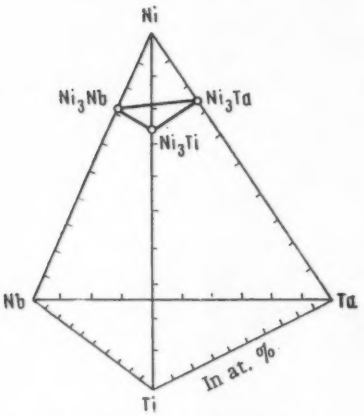

Fig. 1. Quaternary diagram of state Ni–Nb–Ti–Ta.

During an investigation of binary systems between the compounds Ni_3Nb–Ni_3Ta, Ni_3Nb–Ni_3Ti, and Ni_3Ta–Ni_3Ti [2-4] we showed by physicochemical analysis methods the presence of continuous solid solutions. X-ray structure analysis showed that the compounds Ni_3Nb and Ni_3Ta are isostructural; they belong to the structural type β-Cu_3Ti of the rhombic system and form continuous solid solutions with each other [5]. The total solubility of Ni_3Ti–Ni_3Ta–Ni_3Nb, determined by the authors from physicochemical analysis data, indicates the possibility of the existence of a second high-temperature modification of the rhombic system, of the β-Cu_3Ti type [6], for the compound Ni_3Ti, as for the compounds Ni_3Nb and Ni_3Ta. In the literature there are no data on equilibrium in a ternary system of the metallic compounds Ni_3Nb–Ni_3Ti–Ni_3Ta, apart from a general reference to the formation of continuous solid solutions in this system [7].

EXPERIMENTAL

The alloys for the investigation were smelted in an arc furnace with a "permanent" tungsten electrode in a current of argon. Pure metals were used for the preparation of the alloys. The investigation of alloys of the ternary system between the compounds was carried out by methods of thermal analysis, microstructure and hardness for the three polythermal sections passing through the first (radial) from the compound Ni_3Ti to the binary system Ni_3Ta–Ni_3Nb with a 1:1 ratio of the compounds Ni_3Ta: Ni_3Nb, and for the two sections passing through the mimima on the liquidus curves in the corresponding binary systems, which we call $m_1 - m_2$ and $m_2 - m_3$. For the three polythermal sections and for the corresponding binary systems between the compounds, the composition of the alloys investigated were plotted in the form of the points in Fig. 2. For the thermal analysis we used alloys, melted beforehand, corresponding to the exact compositions of the compounds. The cooling curves were recorded by means of a platinum – platinum + 10% rhodium thermocouple in a Kurnakov recording pyrometer.

Fusibility diagrams of the systems. Thermal analysis data, given in Table 1, show that the compound Ni_3Ti has an initial crystallization temperature of 1375°. In the case of the radial section Ni_3Nb–Ni_3Ta with 1:1 ratio of these compounds, addition of Ni_3Ti to the alloy first reduces the crystallization temperature to 1320°, forming a minimum in the ternary system at 80-90% of the total added compounds Ni_3Nb + Ni_3Ta. Subsequently, the crystallization temperature of the alloys gradually increases, reaching 1400° for an alloy with 50% Ni_3Nb and 50% Ni_3Ta.

The crystallization temperature of the alloys of the two sections passing through the minimum in the binary systems varies from 1300 to 1420°. From the thermal analysis data, the fusibility diagrams of the three sections of the ternary system have the appearance of continuous solid solutions with a minimum of the crystallization temperature of about 20% of the sum of the compounds, similar to the fusibility diagrams of the binary systems between

metallides (as shown in Fig. 3). The sections passing through the minima in the binary systems $m_1 - m_2$ and $m_2 - m_3$ are similar to each other (Fig. 4). On the basis of thermal analysis data for the three binary diagrams of state, forming the ternary diagram, and for the three polythermal sections of the ternary system, we plotted the liquidus surface of the ternary systems; it consists of one field of the primary crystallization of the continuous ternary solid solution of metallides of the system $Ni_3Nb + Ni_3Ta + Ni_3Ti$.

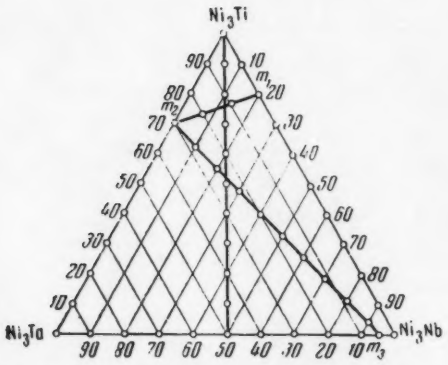

Fig. 2. Compositions of investigated alloys of the system $Ni_3Nb-Ni_3Ti-Ni_3Ta$.

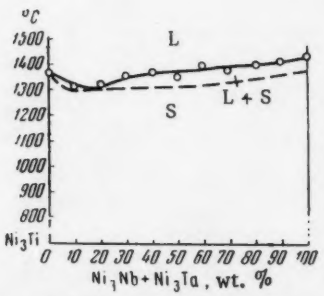

Fig. 3. Radial section of the diagram of state of the ternary system $Ni_3Nb-Ni_3Ta-Ni_3Ti$.

Data of the Thermal Analysis and Hardness of Alloys of the Ternary System

Composition with respect to synthesis, wt. %			Crystallization temp., °C	Hardness H_v, kg/mm²		Characteristic of the sections
Ni_3Ti	Ni_3Ta	Ni_3Nb		cast alloys	annealed alloys	
100	0	0	1375	433	417	
90	5	5	1320	446	425	
80	10	10	1320	459	400	Radical
70	15	15	1360	450	375	section 1:1
60	20	20	1370	442	405	
50	25	25	1350	459	—	
40	30	30	1400	493	401	
30	35	35	1380	—	442	
20	40	40	1400	468	401	
10	45	45	1410	450	—	
0	50	50	1440	442	410	
80,0	0	20	1300	—	—	Section
77,0	10	13	1370	370	—	m_1-m_2
73,0	20,0	7,0	1370	366	—	
70,0	30,0	0	1380	356	—	
62,0	28	10,0	1420	376	—	
55,0	25,0	20,0	1400	376	—	Section
47,0	23,0	30,0	1340	376	—	m_2-m_3
40,0	20,0	40,0	1420	237	—	
33,0	17,0	50,0	1330	397	—	
25,0	15,0	60,0	1380	376	—	
18,0	12,0	70,0	1370	397	—	
11,0	9,0	80,0	1380	443	—	
6,0	4,0	90,0	1300	336	—	
0	5	95	1320	—	—	

The diagrams of state of the binary systems forming the ternary system, and the projection of the space diagram of the fusibility of the ternary system between the compound are shown in Fig. 5. The isothermal lines are drawn at invervals of 25° in the concentration triangle. The maximum value of the temperatures of the commencement of crystallization correspond to the compound Ni_3Ta (m. p. 1531°) and the adjacent region of alloys of the ternary system. The minimum crystallization temperature of 1285° is located on the side of the binary system Ni_3Nb–Ni_3Ti and corresponds to the composition of the alloy with 30% Ni_3Nb and 70% Ni_3Ti.

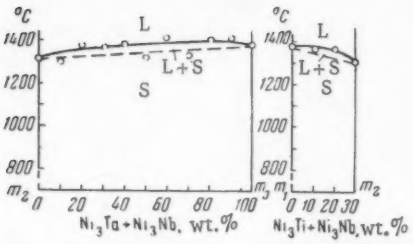

Fig. 4. Thermal diagrams of sections of the system Ni_3Nb–Ni_3Ta–Ni_3Ti, passing through the minimum in binary systems.

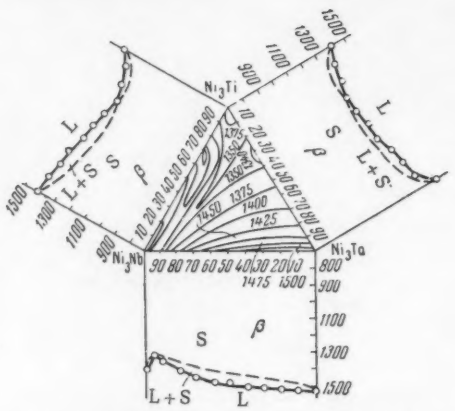

Fig. 5. Fusibility diagram of the ternary system Ni_3Nb–Ni_3Ti–Ni_3Ta.

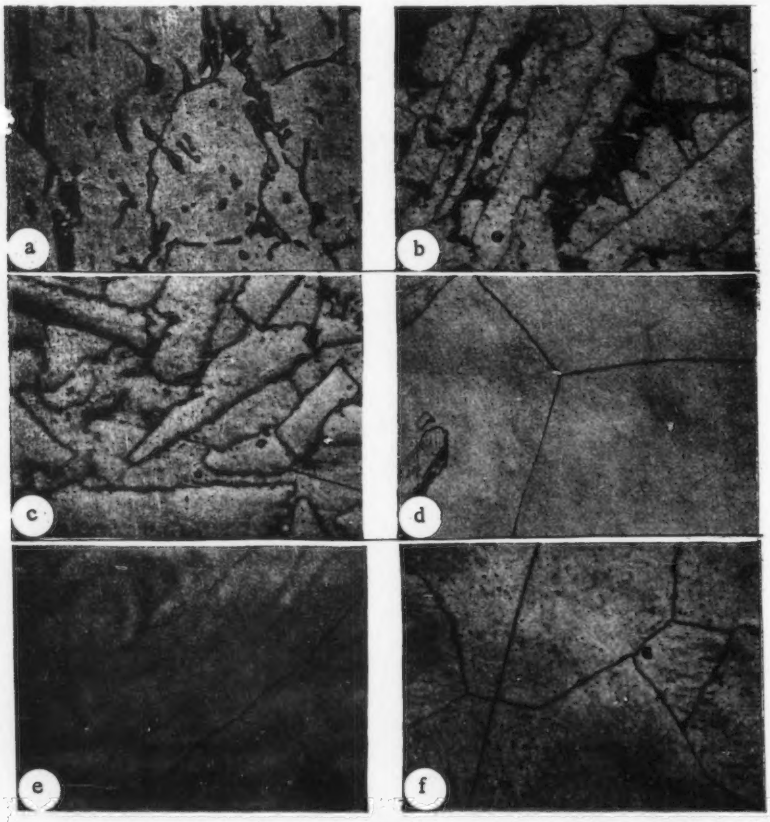

Fig. 6. Microstructure of cast and annealed alloys of the ternary system between metallic compounds (× 200).

Microstructure and hardness of alloys. The presence of solid solutions in a ternary system is confirmed by the investigation of the microstructure of cast and annealed alloys. In the majority of cases the cast structure is dendritic, similar to that shown in Fig. 6a, for an alloy with 15% Ni_3Nb, 15% Ni_3Ta and 70% Ni_3Ti; in Fig. 6b, for an alloy with 17% Ni_3Nb, 33% Ni_3Ti, 50% Ni_3Ta, and in Fig. 6c, for an alloy with 12% Ni_3Nb, 70% Ni_3Ta, and 18% Ni_3Ti. After being annealed at 1200° for 24 hr the microstructure of these alloy compositions is polyhedral (Fig. 6d, e, f).

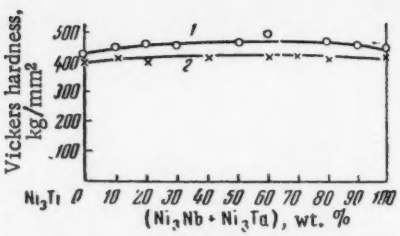

Fig. 7. Hardness of alloys of the ternary system $Ni_3Ta-Ni_3Nb-Ni_3Ti$ for a radial section at a 1:1 ratio of $Ni_3Ta:Ni_3Nb$.

The hardness in the cast and annealed state was investigated for the ternary alloys formed by metallides. The results of the measurements of the hardness of cast and annealed alloys for polythermal sections are given in the table, from which it is seen that the numerical values for cast and annealed alloys varies between 375 and 450 units. The hardness curves of cast and annealed alloys for polythermal sections of ternary compounds (Fig. 7) are characteristic of a continuous series of solid solutions and vary uniformly smoothly with a slight upward convexity, like the graph (Fig. 7) for the section $Ni_3Ti-Ni_3Nb + Ni_3Ta$.

SUMMARY

1. The equilibrium of the ternary system formed by the metallic compounds $Ni_3Nb-Ni_3Ti-Ni_3Ta$ was investigated by physicochemical analysis methods.

2. Alloys of all concentrations of this system crystallize from the fused system in the form of continuous solid solutions.

3. From thermal analysis data of the three binary systems formed by the compounds and the three polythermal sections was plotted the liquidus surface of the ternary system, which consists of one field of primary crystallization of solid solutions of the metallides $Ni_3Nb-Ni_3Ti-Ni_3Ta$.

4. The microstructure of cast and annealed alloys, and the hardness corroborate the thermal analysis data regarding the existence of solutions of metallides in a system of continuous solid solutions.

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A STUDY OF THE NATURE OF THE MICROPOROUS STRUCTURE OF ACTIVE CARBONS

COMMUNICATION 3. ACTIVE CARBONS FROM DIFFERENT CARBONIZED MATERIALS

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Carbonized organic materials of vegetable or fossil origin, used as raw material in active carbon technology, contain greater or lesser quantities of inorganic components which are normally determined analytically in the form of ash. The active carbons obtained from these starting materials contain fairly high quantities of ash, approaching 10% for active carbons based on vegetable raw materials and reaching 30% for active carbons from high-ash brown coals. The de-ashing of active carbons may naturally lead to considerable development of the porous structure.

In the previous studies in this series [1, 2], we examined the microporous structure of practically ashless specimens of active carbons from phenol–aldehyde resin and polyvinylidene chloride and the change in this structure during thermal treatment of the carbons at high temperatures up to 3000°. In the present work, particular attention was paid to the study of the development of the porous structure of active carbons of the industrial type as a result of de-ashing.

In the general case, active carbons are characterized by a polymodal distribution of pore volume, which is fundamental for theories of the different varieties or types of pores: micro, intermediate, and macropores [3]. Sorptive methods make it possible to gain some idea of the volumes, and in some cases of the size distribution of the volumes, of the micro and intermediate pores [3, 4]. The application of these methods to the original and de-ashed active carbons makes it possible to establish the change in the volumes of the micro and intermediate pores as a result of de-ashing. In principle, the change in the macroporous structure could be found from the changes in the curves giving the distribution of the volumes of the macropores according to their effective radii, determined by the mercury impression method. Unfortunately the accuracy of this method is insufficient for the solution of this problem.

In the case of the de-ashed specimens of active carbon, we also estimated the effect of thermal treatment at the highest temperature.

EXPERIMENTAL

The materials studied were two specimens of granulated active carbons prepared under laboratory conditions and an industrial specimen of active carbon. The active carbon C_0-950 was prepared from highly-dispersed carbonized material of vegetable origin with wood resin as binding agent. After granulation, the granules were carbonized in a rotating furnace up to 500° and the carbonized granules were activated with carbon dioxide in the rotating furnace at a temperature of 950° to a degree of charring equal to ~50%. The initial raw material for the preparation of the D-950 carbon was highly-dispersed lean fossil coal with wood resin. The granules were carbonized up to 500° and activated under the conditions described above to a degree of charring equal to ~70%. The third carbon E_0-950 was an industrial specimen of grade F (F-Kohle) active carbon from the Leuna Plant (East Germany), obtained by activating brown coal in a "turbulent layer" at a temperature in the region of 900-950°. This carbon specimen was studied in detail earlier [5].

The carbons were de-ashed by taking portions weighing several grams and treating them twice, successively, with concentrated hydrochloric and hydrofluoric acids in a platinum dish with evaporation to dryness on a water bath. The

specimens were finally washed until free from chloride ion. The de-ashed carbons were dried at 105°. In the above symbols, the subscript "o" is used to distinguish the de-ashed carbons from the original specimens.

The thermal treatment of the de-ashed carbons C-950, D-950, and E-950 was carried out only at the highest temperature in an RS-100 electric resistance furnace under the conditions previously described for the A-3000 carbon [1]. The decrease in weight of the carbons as a result of the thermal treatment was 11.40% for the C-950 carbon, 9.20% for the D-950 carbon, and 24.7% for the E-950 carbon. These carbon specimens are denoted C-3000, D-3000, and E-3000.

The isotherms for the sorption of benzene vapor at 20° over a wide range of equilibrium relative pressures were determined for all these carbon specimens by the vacuum sorptive weight method. The carbons were evacuated beforehand at 450° to a residual pressure of $\sim 1 \cdot 10^{-6}$ mm Hg. Table 1 gives the principal data for the volumes of the different types of pore for the carbon specimens studied.

In contrast to the case of the A-950 carbon from the phenol–aldehyde resin [1] and the B-750 carbon from polyvinylidene chloride [2], thermal treatment of the carbons of the industrial type at 3000° does not lead to complete suppression of their sorptive power. The limiting sorptive volumes for these carbons amounts to several tenths of one cm^3/g, and the C-3000 and E-3000 carbons, but not the D-3000 carbons, exhibit measurable adsorptive properties in the range of relative pressures $1 \cdot 10^{-3} - 1 \cdot 10^{-1}$. The active carbons of series C and E thus have greater thermal stability.

The de-ashing of technically active carbons leads to a fairly marked increase both in the values of the adsorption for characteristic points on the isotherms (a_{mi}, a_s) and in the volumes of the micro and intermediate pores. We shall return later to an analysis of this effect, which is related to dissolution of the ash elements of the carbons.

The isotherm equation from the potential theory of adsorption for adsorbents of the first structural type [6] was applied to the experimental isotherms:

$$a = \frac{W_0}{\underline{v}} e^{-B\frac{T^2}{\beta^2}(\log p_s/p)^2} \qquad (1)$$

where W_0 is the limiting volume of the adsorption space; $\underline{v}$ the volume of 1 mM of adsorbed substance in the liquid form; B the equation constant, which depends on the dimensions of the micropores having a determining influence on the effect of increase in the adsorption potentials, and β the affinity coefficient of the characteristic curves. For benzene, as for standard vapor, $\beta = 1$.

TABLE 1. Constants of the Adsorption Isotherm Equation

Carbon	a_{mi}, mM/g	a_s, mM/g	v_{mi}, cm^3/g	v_{int}, cm^3/g	v_s, cm^3/g
C_0-950	4,06	5,97	0,361	0,169	0,530
C-950	4,80	7,18	0,426	0,212	0,638
C-3000	0,097	1,55	0,009	0,129	0,138
D_0-950	5,02	5,95	0,446	0,082	0,528
D-950	5,90	7,39	0,524	0,132	0,656
D-3000	0,003	0,708	0,000	0,063	0,063
E_0-950	2,34	10,00	0,208	0,680	0,888
E-950	4,00	16,04	0,355	1,072	1,427
E-3000	0,253	2,39	0,022	0,190	0,212

Table 2 gives values of the constants of Eq. (1) for the carbon specimens studied.

Of the active carbon specimens studied, the C_0-950 and C-950 carbons belong to the first structural type. The remaining specimens belong to a mixed structural type [6], and the range of applicability of the adsorption isotherm Eq. (1) is reduced on the side of higher relative pressures. In this case, however, the values of W_0 can be used to estimate approximately the volumes of the finest micropores of the first structural type. As a result of de-ashing of the carbons, the limiting volumes of the adsorption space W_0 increase considerably.

As in the experiments carried out earlier, thermal treatment of the carbons leads to an increase in the constant B, indicating an increase in the dimensions of the micropores, in spite of the sharp decrease in the limiting volumes

of the adsorption space. The D-3000 carbon belongs to the second structural type and in the case of this carbon the constants of the adsorption isotherm equation for adsorbents of the second structural type [6] have the following values: $W_0' = 0.0021$ cm³/g and $A = 5.12 \cdot 10^{-3}$.

TABLE 2. Constants of the Adsorption Isotherm Equation

Carbon	a_0, mM/g	w_0, cm³/g	$B \cdot 10^6$	Range of applicability, p/p_s
C_0-950	4,33	0,384	0,654	$1 \cdot 10^{-5}$—$1 \cdot 10^{-1}$
C-950	4,98	0,443	0,642	$1 \cdot 10^{-5}$—$2 \cdot 10^{-1}$
C-3000	0,107	0,0093	2,86	$2 \cdot 10^{-3}$—$1,5 \cdot 10^{-1}$
D_0-950	2,82	0,250	0,862	$5 \cdot 10^{-6}$—$1,5 \cdot 10^{-1}$
D-950	3,24	0,288	0,900	$8 \cdot 10^{-6}$—$1 \cdot 10^{-3}$
E_0-950	1,74	0,154	0,531	$1,2 \cdot 10^{-6}$—$6 \cdot 10^{-3}$
E-950	3,18	0,283	0,585	$1 \cdot 10^{-5}$—$6 \cdot 10^{-3}$
E-3000	0,288	0,0256	2,12	$2 \cdot 10^{-3}$—$1,5 \cdot 10^{-1}$

De-ashing of the carbons is accompanied by an increase in the characteristic values of the sorption a_{mi} and a_s and in the corresponding sorptive volumes v_{mi}, v_{int}, and v_s, related to units of carbon mass. This effect may be due both to removal of ash, considered as an inert, coarsely-dispersed ballast, and to the formation of some pore volumes from micro and intermediate pores as a result of the dissolution and extraction of ash elements from the carbons.

If the ash of the carbons is considered as ballast, it is possible, from elementary considerations, to establish the relationship between a property F_0 (mM/g, cm³/g) of the original nonde-ashed carbon with an ash content of P_0% and the property F (mM/g, cm³/g) of the de-ashed carbon with residual ash content P%

$$F = \gamma \cdot F_0 \tag{2}$$

where

$$\gamma = \frac{100 - P}{100 - P_0}. \tag{3}$$

Table 3 gives the values of the volumes of the different types of pore, calculated from formula (2) and denoted by the superscript "o," together with values of the difference Δv between the actual pore volume $\underline{v}$ for the de-ashed carbons and the value of v^0:

$$\Delta v = v - v^0 \tag{4}$$

The values of Δv characterize the increase in the volumes of the corresponding types of pore as a result of de-ashing of the carbons. The values of the pore volumes for the carbons before and after de-ashing were given earlier in Table 1.

TABLE 3. Development of the Pore Volumes as a Result of De-ashing of the Carbons

Series of carbon specimens	P_0, %	P, %	γ	Micropores		Intermediate pores		Limiting sorption volume	
				v^0_{mi}	Δv_{mi}	v^0_{int}	Δv_{int}	v^0_s	Δv_s
C	14,01	0,040	1,163	0,420	0,006	0,197	0,015	0,617	0,021
D	11,88	0,080	1,132	0,505	0,019	0,093	0,039	0,598	0,058
E	28,80	2,08	1,373	0,286	0,069	0,934	0,138	1,220	0,207

For the wood charcoal C the removal of ash as ballast leads to an increase in the limiting sorption volume by 19.5% and to an actual development of the volume of the micro and intermediate pores by 3.3%, most of which corresponds to the intermediate pores. For the other extreme case — the high-ash carbon E — the effect of ash as ballast corresponds to an increase in v_s by 37.7% with a further increase by 14.5% due to the formation of new pores. In this case the actual volume of the micropores increases by 19.5% and the volume of the intermediate pores increases by 12.9% as a result of the extraction of ash impregnations with dimensions typical of these types of pore. The carbon D occupies an intermediate position between the two extreme cases considered. Thus the de-ashing of active carbons may lead to a considerable development of the micro and intermediate porosity.

SUMMARY

1. A study has been made of the development of the structure of the micro and intermediate pores of a series of specimens of active carbons of the industrial type as a result of treatment with hydrochloric and hydrofluoric acids. A considerable increase in the volumes of the micro and intermediate pores is observed only for high-ash original carbons.

2. Thermal treatment of active carbons of the industrial type at a maximum temperature of 3000° does not lead to complete suppression of their sorptive power, in contrast to the case of active carbons from phenol – aldehyde resins and polyvinylidene chloride.

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THE ADSORPTION AND HEAT OF ADSORPTION OF NORMAL ALCOHOLS ON GRAPHITIZED CARBON BLACK

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In [1-5] we studied the heat of adsorption of a number of hydrocarbons (normal and isoalkanes, cyclanes, and aromatics) and the regular features governing the adsorption of these substances on the uniform surface of graphitized carbon black. In the present work in this series we have studied the adsorption and heat of adsorption of hydrocarbon derivatives – the normal alcohols: methanol, ethanol, propanol, and butanol, and have also made a tentative determination of the heat of adsorption of water vapor at high degrees of covering of the surface of channel black.

The adsorption of methanol on graphitized channel black and graphite has already been studied [6-10]. In [10] it was shown that the adsorption of methanol is the same on graphite and on graphitized channel and thermal blacks, within the limits of possible accuracy of the graphs given in the literature; the methanol adsorption isotherm has an undulating shape with two inflections, starting with a sharply concave section. This isotherm shape is characteristic of relatively strong adsorbate–adsorbate interaction [11, 9]. The differential heat of adsorption of methanol on graphitized channel black was measured only in [7], but the data must apparently be regarded as tentative, since the authors of [7] do not give the experimental points. In [6] the heat of adsorption of methanol on graphite was calculated from the isosteres.

The isotherms for the adsorption of water vapor on graphitized carbon black and graphite have been studied in a number of works (see for example [8-10, 12-14]); they have been studied in detail in [10]. It was shown that the adsorption of water on graphitized carbon black is negligibly small, the isotherm is concave throughout the whole range of relative pressures p/p_s and even at values of p/p_s close to unity a compact monolayer is not formed. This was attributed to a particularly weak bond between the water molecules and the graphite surface. The differential heat of adsorption of water on graphitized channel black was studied in [13, 14], and contradictory data were obtained. In [13], high negative values were obtained for the pure heat of adsorption, like the heats of adsorption of water on carbon, determined in [15].

EXPERIMENTAL

The main adsorbent used was "sferon-6" carbon black, as used in [5], i.e., graphitized in an atmosphere of helium at 2800° for 10 min; its specific surface, determined by the BET method from the adsorption of nitrogen vapor, was $s = 89\ m^2/g$. A separate study was carried out with T-1 thermal black obtained from Tesner, graphitized at 3000° for 45 min in an atmosphere of CO; its specific surface, determined by the BET method from the adsorption of nitrogen vapor [16], was $29.0\ m^2/g$. Twice-distilled water was used in the experiments. The constants of the purified alcohols used are given in Table 1.

TABLE 1

Alcohol	d^{20}_4	n_D	Vapor pressure p_s
Methanol	0.7917	–	–
Ethanol	–	1.3615 (20°)	34.6 (16°)
n-Propanol	0.8059	1.3860 (20°)	12.4 (18°)
n-Butanol	–	1.3990 (21°)	3.65 (16°)

As in [1-5], the differential heat of adsorption was measured in a calorimeter with constant heat capacity (1953 model) and the magnitude of the adsorption of the alcohols was measured by means of vacuum liquid capillary microburets [17]. The adsorption of water vapor was measured by the gas volume method [18]. The experiments were carried out at 20°; the determination of the isotherm for butanol adsorption was also carried out at 41.5°.

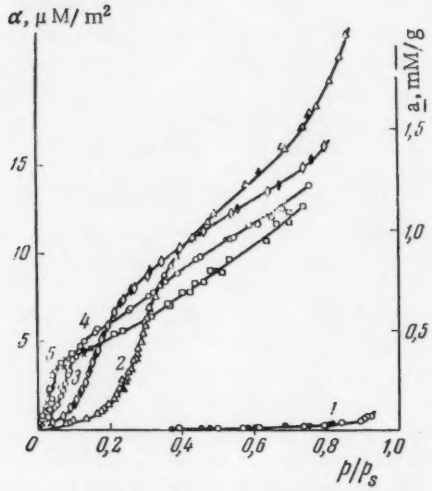

Fig. 1. Isotherms for the adsorption of the vapor of water (1), methanol (2), ethanol (3), propanol (4), and butanol (5) on "sferon-6" graphitized carbon black at 20° (the crosses denote data for the adsorption of butanol at 41.5°; the black symbols give the desorption data).

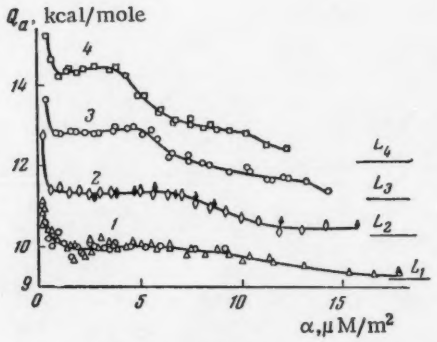

Fig. 2. Relationship between the differential heat of adsorption of the vapor of methanol (1), ethanol (2), n-propanol (3), and n-butanol (4) and the quantity adsorbed on "sferon-6" graphitized carbon black at 20° (the points on curve (1), marked with circles, refer to the heat of adsorption of methanol vapor on graphitized thermal carbon black; the horizontal lines on the right mark the values of the latent heat of condensation of the corresponding alcohols; the black points give the heat of desorption).

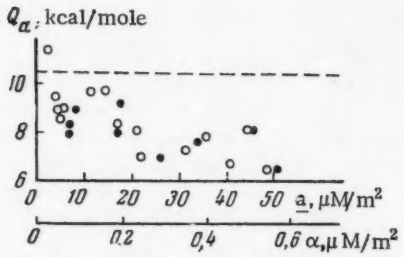

Fig. 3. Relationship between the differential heat of adsorption of water vapor on the quantity adsorbed on "sferon-6" graphitized carbon black at 20° (the black points denote the heat of desorption; the broken line gives the latent heat of condensation of water vapor).

Figure 1 shows the isotherms obtained for the adsorption of the vapor of water, methanol, ethanol, propanol, and butanol on "sferon-6" graphitized carbon black. Several series of experiments were carried out for each vapor and good agreement was obtained. The adsorption isotherms are completely reversible up to very small values of p/p_s. In addition to the relative scale of values of the adsorption a (mM per 1 g), Figure 1 gives the absolute scale α (μM per 1 m^2 of surface).

The adsorption of water is negligibly small and the isotherm is concave throughout. On going from water to methanol the adsorption increases sharply and the isotherm changes shape: remaining concave at first, it subsequently shows two points of inflection. The same isotherm shape is retained for the adsorption of ethanol and propanol (we have not yet established the exact shape of the initial section of the isotherm for butanol, due to the very low values of p). Thus in the alcohol series there is an increase in the adsorption in the initial section of the isotherm with increase in the number n of carbon atoms in the molecule. In the central region the adsorption isotherms cross one another and afterwards the reverse order of values of the adsorption is observed.

Figure 2 shows the relationship between the differential heat of adsorption Q_a and α for the vapors of methanol, ethanol, propanol, and butanol. In the case of ethanol, propanol, and butanol, only "sferon-6" graphitized carbon

black was used, but in the case of methanol, graphitized thermal black with more uniform surface was also used. The heats of adsorption for the two carbon blacks were found to be very close. The heats of adsorption of methanol on graphitized carbon black, measured in [7], are slightly higher than our data, but the heats of adsorption of methanol on graphite, calculated from the isosteres in [6], are close to our data, with the exception of the initial region.

Figure 2 shows that the heat decreases during the adsorption of the first portions of vapor, after which the heat of adsorption either remains constant for a prolonged period (methanol and ethanol) or even increases slightly (propanol and butanol); the heat of adsorption then decreases to values close to the heat of condensation L. The heat of adsorption of the alcohols increases with increase in n. Figure 3 shows the relationship between Q_a and α for water vapor on "sferon-6" graphitized carbon black. Because of the low values of α and Q_a, the accuracy of these experiments is much lower, and this has produced a high scatter in the experimental points. The adsorption of water on carbon black is so small that the correction, determined in blank experiments, for the adsorption on the internal parts of the apparatus amounted to 30%. Figure 3 shows, however, that the differential heat of adsorption of water vapor is undoubtedly much less than L. Comparison of our data with the data of [13] shows good agreement.

The Thermodynamics of the Adsorption of Alcohols on Graphitized Carbon Black

The adsorption isotherm equations. The vapor adsorption isotherms which begin with a concave section are not described by the BET equation, because of the relatively important part played by the adsorbate–adsorbate interaction [11]. In our case this equation cannot describe a sufficiently large section of the adsorption isotherms for methanol and ethanol. The range of applicability of the BET equation increases with increase in n and with increase in the relative part played by adsorbate–adsorbent interaction. Thus the propanol adsorption isotherm, which is concave initially only over an extremely small range of values of p/p_s, and the butanol adsorption isotherm, again with the exception of the initial section, are described satisfactorily by this equation.* The constants of the BET equation, obtained in the calculation, i.e., a_m – the capacity of the monolayer, $\omega_m = 1/\alpha_m$ – the area corresponding to one molecule in the compact monolyaer, and C – the equilibrium constant, are given in Table 2, together with the range of values of p/p_s and of degree of covering θ for which this equation is applicable. Thus the BET equation made it possible to estimate ω_m for propanol and butanol. The values of ω_m correspond to planar orientation of the alcohol molecules on the graphite surface.

We next tried to calculate, by an independent method, the areas of projection of the alcohol molecules on the plane of the adsorbent surface, assuming that they exhibit planar orientation relative to this surface and making allowance for the van der Waals dimensions. The following values were used in the calculation: van der Waals radii of the atoms C 1.7 A, O 1.5 A, and H 1.2 A; interatomic distances C–C 1.54 A, C–H 1.1 A, C–O 1.4 A, and O–H 1.2 A; and valence angles C–C–C, H–C–C, and C–O–H approximately 110°. The values of the areas of projection of the isolated molecules CH_3OH, C_2H_5OH, C_3H_7OH, and C_4H_9OH, obtained from these data, were 17, 22, 28, and 33 A^2 respectively. The shape of the adsorption isotherms and the values obtained for the heats of adsorption of the alcohols, which are much greater than the heats of adsorption of the corresponding hydrocarbons [3], indicate, however, that in the adsorption layer there are hydrogen bonds joining the alcohol molecules at the shortest distance. To make allowance for this we took the O–H···O distance as 2.6 A and the H–O···H angle as 110°. As a result of the effect of the hydrogen bonds, the alcohol molecules approach much closer to one another and for a pair of alcohol molecules joined by one hydrogen bond, the area of projection is smaller, by approximately 4 A^2, than that for two isolated molecules.** In a layer of alcohol molecules joined by hydrogen bonds, there is one hydrogen bond for every molecule, i.e., the area of projection of an isolated alcohol molecule should be reduced by 4 A^2. Even when the alcohol molecules are packed together as closely as possible on the surface, however, gaps remain between them; calculation shows that the actual value of the areas occupied by the molecule in the adsorption layer should exceed their calculated areas of projection on the plane by approximately 15-20%. Thus one molecule of alcohol in the monolayer formed by molecules joined to one another by hydrogen bonds is associated with the following areas: 16 16 A^2 for methanol, 22 A^2 for ethanol, 29 A^2 for propanol, and 36 A^2 for butanol.*** The value of ω_m = 16 A^2 for methanol is close to that obtained in [6, 9]. For propanol and butanol the calculated values are close to those found above by the BET method (see Table 2).

A^2 for butanol.*** The value of ω_m = 16 A^2 for methanol is close to that obtained in [6, 9]. For propanol and butanol the calculated values are close to those found above by the BET method (see Table 2).

*The Langmuir and BET equations represent the limiting case of the more general equations of localized adsorption, which take account of adsorbate–adsorbate interaction [11]; their applicability is greater, the less marked the adsorbate–adsorbate interaction compared with the adsorbate–adsorbent interaction.

**For the same reasons, the volume corresponding to a single molecule of alcohol in the liquid is slightly less than that for the corresponding hydrocarbon. Thus for butanol and n-butane these values at 20° are ~151 and 160 A^3.

***It is possible that these values are minimum values, due to the thermal movement of the molecules in the adsorption layer.

In the subsequent calculations of the values of $\theta = (\alpha / \alpha_m = \alpha\omega_m)$, ω_m: 16 and 22 A^2, and for propanol and butanol we took the values obtained by the BET method (see Table 1): 28.2 and 35.3 A^2.

TABLE 2. Constants of the BET Equation and the Limits of Its Applicability for the Adsorption of Alcohols on Graphitized "sferon-6" Carbon Black

Adsorbate	α_m, $\mu M/m^2$	ω_m, A^2	C	Limits of applicability	
				of p/p_s values	of the values of θ
n-Propanol	5.9	28.2	18	0.1 -0.35	0.7-1.4
n-Butanol	4.7_2	35.3	38	0.05-0.5	0.6-1.9

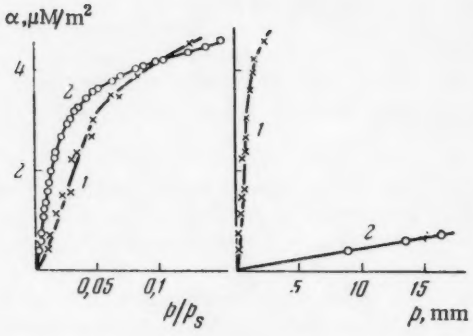

Fig. 4. Adsorption isotherms for the vapors of n-butanol (1) and n-butane (2) on graphitized "sferon-6" carbon black at 41.5°. Left – as a function of p/p_s; right – as a function of p.

The values of ω_m increase by 6-7 A^2 on going from a lower alcohol to a higher alcohol. This increment is close to that observed for n-alkanes, where the increase in ω_m per CH_2 group is 5-6 A^2. The extremely compact arrangement of alcohol molecules in the monolayer should be noted. Figure 4 gives a comparison of the adsorption isotherms as functions of p/p_s and p for the adsorption of butane [19] and butanol on graphitized channel black, recorded at the same temperature of 41.5°. Figure 4 shows that in the initial section of the isotherms the adsorption of butanol for a given relative vapor pressure p/p_s is less than the adsorption of butane, corresponding to the lower pure heat of adsorption of the alcohol. The isotherms are close together in the range corresponding to covering by the monolayer. In accordance with the fact that the total heat of adsorption of butanol is greater than that of butane (as a result of the strong adsorbate–adsorbate interaction), the adsorption isotherm, as a function of the absolute vapor pressure p for butanol, rises much more steeply than that for butane.

For a more complete description of the isotherms for the adsorption of alcohols on graphite than is given by the BET method, it is necessary to take account of the adsorbate–adsorbate interaction. We therefore used the more general approximate equation for localized adsorption on a uniform surface [11, 20]:

$$\frac{\theta(1-p/p_s)^2}{p/p_s[1-\theta(1-p/p_s)]} = K_1' + K_1'K_n\theta(1-p/p_s), \qquad (1)$$

where K_1' and K_n are the equilibrium constants characterizing the adsorbate–adsorbent and adsorbate–adsorbate interactions; where $K_n = 0$ this equation becomes the BET equation. The values obtained for the constants of Eq. (1) are given in Table 3.

TABLE 3. The Constants of the Equation for Polymolecular Adsorption, with Allowance for the Adsorbate–Adsorbate Interaction, for the Adsorption of Alcohols on Graphitized Carbon Black

Adsorbate	Value taken		$K_1'K_n$	K_1'	K_n
	ω_m, A^2	α_m, $\mu M/m^2$			
Methanol	16	10,4	4	0,04—0,1	35—100
Ethanol	22	7,5	11	0,2	55
Propanol	28,2	5,9	22	0,4	55
Butanol	35,3	$4,7_2$	50	1	50

Table 3 shows that in the alcohol series the product of the constants $K_i^1 K_n$, a quantity which can be determined most accurately [the slope of the straight line in the graph of Eq. (1)], increases with increase in n. The accuracy of the calculation of the constant K_i^1 characterizing the adsorbate–adsorbent interaction is low, due to the low value of the constant for the adsorption of alcohols on graphitized carbon black. The inaccuracy in the determination K_i^1 leads to inaccuracy in the determination of the constant K_n. It is still possible, however, to observe a tendency for K_i^1 to increase and for the value of K_n to remain constant, with increase in n. The isotherms for the adsorption of the alcohols, calculated from Eq. (1), with the values of the constants given in Table 3, are compared with the experimental data in Fig. 5. The best agreement with the equation is shown in the case of the adsorption of butanol.

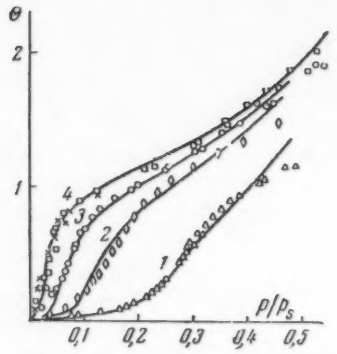

Fig. 5. Isotherms for the adsorption of the vapors of methanol (1), ethanol (2), propanol (3), and butanol (4) on graphitized "sferon-6" carbon black. [The points give the experimental data and the curves are calculated from Eq. (1)].

It should be noted that on going from the graphitized channel black "sferon-6" (2800°) with less uniform surface to the graphitized thermal black T-1 (3000°), there is a decrease in the localization of the alcohol molecules. The isotherm for the adsorption of methanol on graphitized thermal black with uniform surface is more satisfactorily described by Hill's equation for nonlocalized adsorption [21]. Thus, increase in the degree of uniformity of the surface leads in this case to delocalization of the methanol molecules [22].

The relationship between the heat of adsorption and the degree of covering of the surface. The appearance of a maximum value of Q_a close to completion of the monolayer on going from methanol to butanol (Fig. 2) may be attributed to an increase in the dispersion attraction between the hydrocarbon parts of the alcohol molecules with increase in n. The interaction of the hydroxyl groups of the alcohols, however, is not revealed in the form of maxima on the heat of adsorption curves, apparently because of the fact that, as a result of the much higher energy, this interaction takes place even during the adsorption of the first portions of alcohol and continues until the adsorption process is complete. The increase in the heat of adsorption at lower values of θ, however, is masked by the residual nonuniformity of the surface. This can be seen by comparing the heats of adsorption of butane and butanol. The molecules of these two substances contain the same number of C and H atoms, and since the energy of the dispersion interaction between the oxygen atom and graphite and the polarization of the graphite by the OH dipole are relatively low, the energy of adsorption of an isolated butanol molecule on graphite should not be much greater than the energy of adsorption of the butane molecule. At the same time the differential heats of adsorption Q°_a on "sferon-6" carbon black (2800°) at standard degree of covering θ = 0.5 differ considerably. For butane Q°_a = 8.4 kcal/mole and for butanol Q°_a = 14.4 kcal/mole. This difference also corresponds approximately to the energy of the hydrogen bond between two alcohol molecules.

We have already made a theoretical estimation (see [23]) of the energy of adsorption of alcohols on graphite [24].

Free energy and entropy of adsorption. The isotherms for the adsorption $\alpha\ (p/p_s)$ and differential heat of adsorption $Q_a(\alpha)$ were used, as in [1-5], to determine the dependence on θ of the differential changes in the total energy $\partial \Delta u/\partial \alpha = -(Q_a - L)$, free energy $\Delta\mu = RT \ln p/p_s$, and entropy of adsorption $\partial \Delta s/\partial \alpha = 1/T\ (\partial \Delta u/\partial \alpha - \Delta\mu)$ on going from the pure liquid to the adsorption layer.

Figure 6 shows that the shapes of the $\partial \Delta u/\partial \alpha$ and $\Delta\mu$ for all the alcohols are very similar. In the case of the alcohols, in contrast to the case of the hydrocarbons, the values of the total and free energies (for the choice of standard state made) are very close to one another; for methanol the difference lies within the limits of experimental error. The curves giving the relationship between the differential entropy of adsorption and the degree of covering of the surface for ethanol, propanol, and butanol are given in Fig. 7. This figure also gives for comparison the entropy curve for n-butane, calculated from the data given in [19]. The general shape of the curves is the same as in the case of the n-alkanes, i.e., the beginning of the curves lies in the range of positive values; subsequently, they move into the range of negative values (relative to the entropy of the liquid). The entropy curves pass through a minimum at about θ = 0.9, after which they approach zero (the entropy of the liquid) at about θ = 1.1. In the case of alcohols, however, the absolute value of the differential change in entropy is much less than that for the n-alkanes. In the case of methanol and ethanol the differential change in entropy, throughout the whole range of covering by the monolayer, is

close to zero. In the case of propanol and butanol, there is only a comparatively weakly-defined minimum close to completion of the monolayer. This indicates that the state in the monolayer is very close to the state in the ordinary liquid, which is also determined to a considerable extent by hydrogen bonding between the molecules. It is only in the case of the higher alcohols, close to completion of the monolayer, that, as a result of the ordering process, there is a considerable decrease in the entropy, associated with the interaction of the hydrocarbon parts of the molecules.

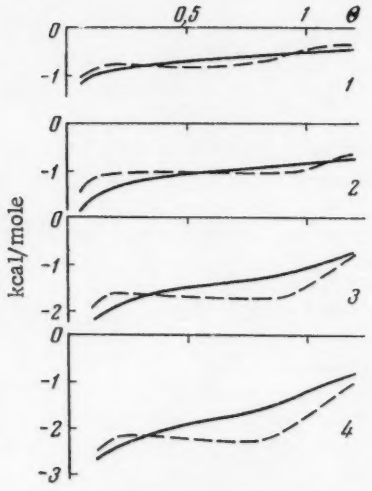

Fig. 6. Dependence of the differential change in the total energy (broken lines) and free energy (solid lines) on the degree of covering of the surface of graphitized carbon black for the adsorption of methanol (1), ethanol (2), propanol (3), and butanol (4).

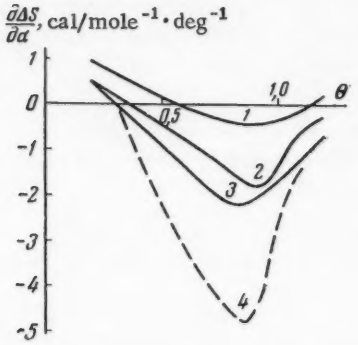

Fig. 7. Dependence of the differential change in the entropy of adsorption of ethanol (1), propanol (2), butanol (3) and butane (4) on the degree of covering of graphitized "sferon-6" carbon black.

Standard thermodynamic characteristics of the adsorption of alcohol vapors on graphitized channel black. Table 4 gives the standard values (for $\theta = 0.5$) of the differential heats of adosprtion, total and free energy and entropy of adsorption.

The standard values of the heats of adsorption increase on going from methanol to butanol, and the increment in the heat of adsorption ΔQ°_a on going from one to the other increases slightly, but this increment in the case of the alcohols is much less than that for the n-alkanes: in the n-alkane series studied, it has a constant value of 1.9 kcal/mole from n-butane to n-octane [3].

The fact that the increment in the heat of adsorption in the case of the alcohols is not constant and does not coincide with the value for n-alkanes is apparently due firstly to the fact that we studied the first members of the alcohol series and secondly to the fact that the existence of the interaction of the hydroxyl groups of the alcohols with one another may lead to an arrangement of alcohol molecules on the surface, which is energetically slightly less favorable for adsorbate–adsorbent interaction than that for the case of n-alkane molecules.

An analogous change in the increment is observed for $\Delta\mu^\circ$.

Comparison of the standard thermodynamic quantities for the adsorption of methanol on graphitized channel carbon black, the original (oxidized) carbon black, and hydrated silica gel. It was considered of interest to compare the adsorption characteristics for a given adsorbate on adsorbents with different surface structures. It was possible to make this comparison for methanol, for which the heats of adsorption on the original channel black [25] and on silica gel [26] have also been determined. It is known that graphitized carbon black, consisting of pure carbon which is present for the most part in the lattice of crystallites which reach considerable dimensions, exhibits a very uniform surface. The original channel black, consisting of small crystallites and amorphous particles, is rough and extensively oxidized, and some of the oxygen compounds on the surface are capable of reacting to form hydrogen bonds [27]. The particles forming the skeleton of hydrated silica gel form hydrogen bonds with alcohol molecules. Under certain conditions the alcohols may react chemically with the silica to form esters [28, 29].

Table 5 gives the standard (at $\theta = 0.5$) thermodynamic characteristics for the adsorption of methanol or graphitized channel black, the original (oxidized) "sferon-6" carbon black heated in vacuum only at 900°, and hydrated silica gel.

Table 5 shows that on going from graphitized channel black to the original oxidized carbon black and hydrated silica gel, in the case of the alcohol, all the standard thermodynamic quantities become more negative, in contrast to the case of the n-alkanes [30]. The high negative change in the entropy of adsorption indicates a relatively marked decrease in the mobility of the methanol molecules in the surface layer on the last two adsorbents.

The authors wish to thank P. A. Tesner for providing the highly-dispersed thermal black and K. D. Scherbakova and V. L. Foss for providing the purified reagents.

TABLE 4. Standard Thermodynamic Characteristics of the Adsorption of n-Alcohol Vapors on Graphitized Carbon Black at 20°

Absorbate	Q_a°, kcal/m	ΔQ_a°, kcal/m	$\left(\frac{\partial \Delta u}{\partial \alpha}\right)^\circ$, kcal/m	$(\Delta\mu)_\alpha^\circ$, kcal/m	$\Delta(\Delta\mu)^\circ$, kcal/m	$\left(\frac{\partial \Delta s}{\partial \alpha}\right)^\circ$, cal/m.deg
Methanol	10,0	1,3₅	−0,8	−0,7₃	0,3₇	−0,₃
Ethanol	11,3₅	1,5₀	−1,0₅	−1,1₀	0,4₀	+0,₂
Propanol	12,8₅	1,5₅	−1,6₅	−1,5₀	0,4₅	−0,5
Butanol	14,4₀		−2,2₅	−1,9₅		−1,0

TABLE 5. Standard Thermodynamic Characteristics of the Adsorption of Methanol on Graphitized Channel Black, the Original Oxidized Carbon Black, and Hydrated Silica Gel

Adsorbent	$\left(\frac{\partial \Delta u}{\partial \alpha}\right)^\circ$, kcal/mole	$(\Delta\mu)^\circ$, kcal/mole	$\left(\frac{\partial \Delta s}{\partial \alpha}\right)^\circ$, cal/m.deg
Graphitized channel black	−0,8	−0,7₃	−0,₃
Original oxidized carbon black [25]	−3,3	−1,7	−5,4
Hydrated silica gel [26]	−5,1	−3,1	−6,8

SUMMARY

1. The adsorption isotherms and the differential heats of adsorption of the vapors of water, methanol, ethanol, n-propanol, and n-butanol on graphitized channel carbon black have been determined; the heat of adsorption of water vapor is much less than the heat of condensation, and the heats of adsorption of the alcohols increase with increase in the length of the carbon chain.

2. The values of the heats of adsorption and the areas corresponding to a molecule of the alcohols in the compact monolayer on the surface of graphitized carbon black indicate that the alcohol molecules are arranged parallel to the surface and form hydrogen bonds with one another.

3. The standard thermodynamic characteristics of the adsorption of n-alcohols on graphitized channel black have been determined and it has been shown that the state of a substance in the adsorption layer in these cases is close to the associated state in the liquid.

4. On going from adsorption on graphitized carbon black to adsorption on the original (oxidized) carbon black, and more particularly to adsorption on silica gel with a hydrated surface, there is a sharp increase in the localization of methanol molecules.

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THE BONDING ENERGIES OF THE ATOMS OF REACTING ORGANIC SUBSTANCES WITH THE CATALYTICALLY ACTIVE CENTERS OF TITANIUM DIOXIDE

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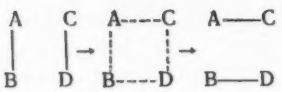
Many catalytic reactions proceed through an intermediate multiple complex, most often a double one



For these reactions we have [1, 2]

$$E = -Q_{AB} - Q_{CD} + Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK}, \quad (1)$$

where E is the height of the energy barrier for the reactions: Q_{AB}, Q_{CD} are the magnitudes of the bonding energies broken during the reaction; Q_{AK}, Q_{BK}, Q_{CK}, Q_{DK} are the magnitudes of the energies of the bonds which are formed by the atoms of the molecules with the catalyst; K is the catalyst.

Equation 1 is jusitifed for cases when the limiting stage of the catalytic reaction is the adsorption of the initial substances. The quantities Q_{CK}, Q_{HK}, Q_{OK} are found by solving a system of three equations of type 1 (see Eqs. 3-5) for the reactions of dehydrogenation of hydrocarbons and alcohols and of dehydration of alcohols, taking into consideration the relations

$$E = -\frac{4}{3}\varepsilon \quad (2)$$

$$Q_{CK} = {}^1/_3(-\varepsilon_1 + 2\varepsilon_2 - 2\varepsilon_3) + 36{,}7 \quad (3)$$

$$Q_{HK} = {}^1/_3(-\varepsilon_1 - 2\varepsilon_2 + 2\varepsilon_3) + 62{,}0 \quad (4)$$

$$Q_{OK} = {}^1/_3(3\varepsilon_1 - 2\varepsilon_2 - 2\varepsilon_3) + 48{,}8 \quad (5)$$

The thermochemical values of the bond energies (kcal/M) [3, 4] were used for the calculations: $Q_{CH} = 98{,}7$; $Q_{CO} = 85{,}5$; $Q_{OH} = 110{,}8$. The quantities Q_{AK}, Q_{BK}, Q_{CK}, Q_{DK} are affected both by the substituents of the reacting atoms (layer IV in the multiple complex) [5,6] and by the atoms surrounding the catalytically active centers of the surface of the catalyst (layer I in the multiple complex). The energy of the bond at the active center Q_{AK}, is equal to

$$Q_{AK} = Q^{\circ}_{AK} + \lambda_A, \quad (6)$$

where Q°_{AK} is the energy of the A-K bond inside the lattice of the catalyst; λ_A is a sublimation term conveying all the influence of the neighboring atoms of the catalyst on the active center. The sublimation term is a complex quantity: it may be positive or negative, depending on the nature, number, and distribution of atoms close to the catalytically active part [7].

In the preceding communication [8], we discussed the influence of the method of preparation of the titanium dioxide on its catalytic properties in reactions with alcohols and hydrocarbons. The influence of the method of preparation on the magnitudes of the bond energies of the catalyst with the atoms of the reacting molecules is demonstrated in this work. The bond energies of each of 4 catalysts and the adsorption potential q [2] are given in Tables 1-4. From these tables it follows that the magnitudes of the bond energies are influenced by the method of preparation of the catalyst and by the structure of the reacting substance. The quantity Q_{OK} is changed most, which is in agreement with data for other oxide catalysts [9]. From Tables 1-4, it is apparent that the values of Q_{CK} for each of the four samples of titanium dioxide often exceed 30.0 kcal/M. Such values of Q_{CK} obviously indicate strong adsorption of the reacting substance, which apparently is the cause of the susceptibility of titanium dioxide to carbonization during the reaction; this leads to a change in the direction of the reaction in the case of isopropyl alcohol [10]. The values of Q_{CK} for cerium and chromium oxides do not exceed 23.0 kcal/M, and, indeed, carbon formation on these catalysts occurs to a smaller degree; the carbonaceous precipitate which is formed does not change the direction of the reaction with isopropyl alcohol.

TABLE 1. The Influence of the Method of Preparation of TiO_2 Catalyst on the Magnitudes of the Bond Energies

Catalyst	Reaction	ϵ, kcal/M	Q_{HK}	Q_{CK}	Q_{OK}	q_1	q_2	q_3
1. Prepared from hydrated titanium oxide obtained by the hydrolysis of $TiCl_4$ with distilled water.	The dehydrogenation of C_6H_{12}	19.0						
	The dehydrogenation of C_2H_5OH	22.8	57.1	29.0	35.9	172.2	179.1	151.0
	The dehydration of C_2H_5OH	25.0						
2. Prepared by precipitation of hydrated titanium oxide with a weak solution of ammonia and subsequent dehydration of the hydrated oxide.	The dehydrogenation of C_6H_{12}	14.7						
	The dehydrogenation of C_2H_5OH	20.4	60.5	28.6	33.0	178.2	182.6	150.7
	The dehydration of C_2H_5OH	25.3						
3. Prepared by oxidation in air of the hydrated titanium oxide obtained by precipitation from $TiCl_3$ with ammonia and subsequent dehydration of the hydrated oxide.	The dehydrogenation of C_6H_{12}	21.6						
	The dehydrogenation of C_2H_5OH	9.4	53.1	31.3	59.5	168.8	197.0	175.2
	The dehydration of C_2H_5OH	6.9						
4. Prepared by the hydrolysis of orthoethyltitanium with distilled water and subsequent dehydration of the hydrated oxide	The dehydrogenation of C_6H_{12}	15.0						
	The dehydrogenation of C_2H_5OH	12.4	57.1	31.7	47.2	177.6	193.1	167.7
	The dehydration of C_2H_5OH	12.5						

TABLE 2. Bond Energies on Partially Carbonized Catalyst 1

Reaction	ϵ, kcal/M	Q_{HK}	Q_{CK}	Q_{OK}	q_1	q_2	q_3
The dehydrogenation of C_6H_{12}	19.0						
The dehydrogenation of C_2H_5OH	22.8	57.1	29.0	35.9	172.2	179.1	151.0
The dehydration of C_2H_5OH	25.0						
The dehydrogenation of C_6H_{12}	19.0						
The dehydrogenation of C_2H_5OH	22.8	56.7	29.4	36.3	172.2	179.1	151.8
The dehydration of $i\text{-}C_3H_7OH$	24.4						
The dehydrogenation of 1,4-cyclohexadiene	22.3						
The dehydrogenation of C_2H_5OH	22.8	56.0	27.9	39.2	167.8	179.1	151.0
The dehydration of C_2H_5OH	25.0						

TABLE 2 (continued)

Reaction	ε, kcal/M	Q_{HK}	Q_{CK}	Q_{OK}	q_1	q_2	q_3
The dehydration of cyclohexene	25.0						
The dehydrogenation of C_2H_5OH	22.8	55.2	27.0	41.9	164.4	179.1	151.1
The dehydration of C_2H_5OH	25.0						
The dehydrogenation of C_6H_{12}	19.0						
The dehydrogenation of n-C_3H_7OH	19.4	50.8	35.4	46.8	172.4	183.8	168.4
The dehydration of n-C_3H_7OH	12.1						
The dehydrogenation of cyclohexene	25.0						
The dehydrogenation of n-C_3H_7OH	19.4	48.8	33.4	52.8	164.4	183.8	168.4
The dehydration of n-C_3H_7OH	12.1						
The dehydrogenation of 1,4-cyclohexadiene	22.3						
The dehydrogenation of n-C_3H_7OH	19.4	49.7	34.2	50.1	167.8	183.7	168.2
The dehydration of n-C_3H_7OH	12.1						

TABLE 3. Bond Energies on Partially Carbonized Catalyst 2

Reaction	ε, kcal/M	Q_{HK}	Q_{CK}	Q_{OK}	q_1	q_2	q_3
The dehydrogenation of C_6H_{12}	14.7						
The dehydrogenation of C_2H_5OH	20.4	60.5	28.3	32.8	177.6	182.1	149.9
The dehydration of C_2H_5OH	25.3						
The dehydrogenation of C_6H_{12}	14.7						
The dehydrogenation of i-C_3H_7OH	10.4	60.5	28.6	46.3	178.2	195.9	164.0
The dehydration of i-C_3H_7OH	15.3						
The dehydrogenation of C_6H_{12}	14.7						
The dehydrogenation of C_2H_5OH	20.4	53.7	35.6	38.9	178.6	181.9	163.8
The dehydration of i-C_3H_7OH	15.3						

TABLE 4. Bond Energies on Partially Carbonized Catalysts 3 and 4

Catalyst No.	Reaction	ε, kcal/M	Q_{HK}	Q_{CK}	Q_{OK}	q_1	q_2	q_3
3	The dehydrogenation of C_6H_{12}	21.6						
	The dehydrogenation of C_2H_5OH	9.4	53.1	31.3	59.5	168.8	197.0	175.2
	The dehydration of C_2H_5OH	6.9						
4	The dehydrogenation of C_6H_{12}	15.0						
	The dehydrogenation of C_2H_5OH	12.4	57.1	31.7	47.2	177.6	188.6	163.2
	The dehydration of C_2H_5OH	12.5						

SUMMARY

1. The magnitudes of the bond energies of the atoms of reacting molecules—hydrogen, carbon, and especially oxygen—depend on the structure of the reacting substances and on the method of preparation of the titanium dioxide.

2. The augmentation of the value of Q_{CK} (for example up to 30.0 kcal per mole and higher) increases carbon formation on the oxide catalyst.

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THE MECHANISM OF THE INITIATING ACTION OF NITROGEN DIOXIDE IN THE OXIDATION OF 2,7-DIMETHYLOCTANE BY MOLECULAR OXYGEN

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It is known that in the beginning stages of the process, the rate of oxidation of hydrocarbons is slow. Often the reaction has a period of induction. For the purpose of accelerating the process of oxidation, the brief application of penetrating radiation or of chemically active gases in the beginning stages of the process of oxidation was suggested [1]. In a series of examples it was shown that such action in the beginning stages of the reaction eliminated completely or sharply diminished the period of induction and led to a significant acceleration of the process. This acceleration, as the result of a transient influence at the beginning stage of the reaction, is based on the fact that the reaction of oxidation develops by a chain mechanism with degenerative branching. The beginning stage is slowest when the concentration of the branching agent in the system is small. One need only accelerate this stage in order to develop a rapid reaction in the system. When a sufficient quantity of the branching agent has accumulated in the system, the catalyst, as a rule, is no longer necessary. Even without it the reaction proceeds rapidly enough. Furthermore, in a number of cases it has turned out that the presence of the catalyst in an already developed reaction generally is undesirable since a greater quantity of side products accumulates, and there is more tar formation from the hydrocarbon which is being oxidized. Following the transient action of penetrating radiation or of chemically active gases during the initial stage, the reaction develops in the absence of a catalyst.

The gaseous initiation effect was observed in the oxidation reactions of hydrocarbons catalyzed by means of a brief insufflation of chemically active gases [2]. However the mechanism of the gaseous initiation was not studied. The present investigation was undertaken for the purpose of illucidating the principle mechanism of the gaseous initiation of the oxidation of hydrocarbons, for example, the oxidation of isodecane (2,7-dimethyloctane).

EXPERIMENTAL

The oxidation of 2,7-dimethyloctane was carried out in a glass oxidizing vessel with a thermostatic jacket through which glycerin was pumped. Oxygen, freed from water vapor, was bubbled through the hydrocarbon. The rate of feed of the oxygen was controlled with a rheometer.

The oxidation vessel was furnished with a sampling tube and a reflux condenser which prevented the removal of the substance by the stream of oxygen. The concentration of peroxidic compounds was determined by the iodometric method in samples removed during the course of the reaction.

The kinetics of the oxygen absorption were measured in a series of experiments. For this purpose, apparatus was assembled which allowed the automatic recording of the volume of oxygen absorbed by the system at constant pressure [3].

The hydrocarbon was synthesized by the Wurtz reaction from isoamyl bromide and purified by the standard method [4]. Nitrogen dioxide was formed directly before insufflation into the oxidation vessel by the mixture of streams of oxygen and nitric oxide. Nitric oxide was obtained by the interaction of $FeCl_3$ with $NaNO_3$ in the presence of HCl and was stored in a gasometer.

The effect of gaseous initiation. In Fig. 1 are presented the kinetic curves of peroxide accumulation during the oxidation of 2,7-dimethyloctane, obtained by a brief (5 min) action of nitrogen dioxide (in mixture with oxygen), and in the absence of the gaseous initiator. As is apparent from Fig. 1, the 5 min initiation substantially accelerated the

reaction. The type of kinetic curve was also changed (transition from an acceleration in the beginning to a constant rate of oxidation); however the limiting concentration of peroxide in the initiated and uninitiated reactions appears to be identical.

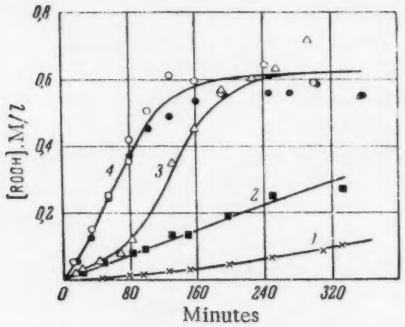

Fig. 1. The kinetics of the accumulation of peroxide during the oxidation of 2,7-dimethyloctane by oxygen at 120° and at 140°. 1,3 – Uninitiated reaction; 2,4 – initiated by NO_2 (10%) during 5 min; 1,2 – 120°; 3,4 – 140°.

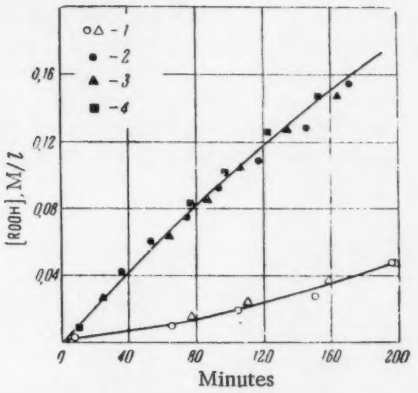

Fig. 2. The kinetics of the accumulation of perioxidic compounds during the oxidation of 2,7-dimethyloctane at 120°. 1 – Uninitiated reaction; 2,4 – after 5 min insufflation with a mixture of NO_2–O_2; 2 – 9% NO_2; 3 – 16% NO_2; 4 – 37% NO_2.

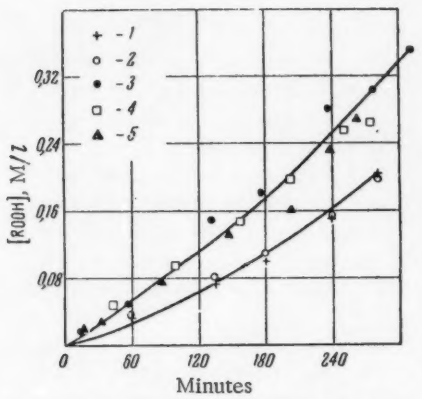

Fig. 3. The kinetics of the accumulation of peroxides during the oxidation 2,7-dimethyloctane at 120° for different periods of initiation. 1) 1 min; 2) 2 min; 3) 5 min; 4) 10 min; 5) 30 min.

In order to select the optimum conditions for carrying out the experiments we investigated the dependence of the gaseous initiation effect on the period of insufflation of the nitrogen dioxide and on its concentration. As is apparent from Figs. 2 and 3, the gaseous initiation effect is practically independent of the concentration of the nitrogen dioxide (in the range 9-37%), and only slightly depends on the period of insufflation. Therefore we subsequently took as the standard a 5 min initiation with a 10-15% mixture of nitrogen dioxide and oxygen.

As a result of the gaseous initiation, not only is the accumulation of peroxidic compounds accelerated, but also the absorption of oxygen (4-5 times at 120°). One ought, however, to observe that we were able to measure the absorption of oxygen only at the very beginning of the reaction. In proportion to the increase of the extent of reaction, the measured rate of oxygen absorption gradually falls; thereafter absorption changes to gas evolution. This effect is connected with the formation during the course of the oxidation of gaseous or low boiling liquid products which by evaporating increase the pressure in the reaction vessel. At the beginning of the reaction 60-80% of the absorbed oxygen is observed in the form of peroxidic compounds.

The mechanism of the initiating action of nitrogen dioxide. The existence of a stable initiator. In principle it is possible to suggest two different mechanisms for the gaseous initiation: 1) the acceleration of the process of oxidation is possible due to an increase in the rate of initiation of chains as a result of the interaction of the chemically active gas with the hydrocarbon; for example, during initiation by nitrogen dioxide according to the reaction $RH + NO_2 \rightarrow R + HNO_2$, where RH is the hydrocarbon and R is the corresponding radical; 2) one could propose that by the interaction of the chemically active gas with the components of the reacting system there is formed a relatively stable catalyst which by some means accelerates the reaction.

In order to make a choice between the two possible general mechanisms, we carried out a series of experiments in which immediately after the 5 min initiation we interrupted the oxidation and maintained the initiated hydrocarbon for several hours at room temperature. On continuation of the oxidation after the interruption, the kinetic curve of the accumulation of peroxide exactly coincided with the standard curve without the interruption corresponding to the temperature of the experiment. If the acceleration of the reaction were connected with the direct initiating action of the nitrogen dioxide, then the interruption should have led to a slowing of the reaction. The rapid course of the reaction after the interruption cannot be explained by proposing that a branching agent—peroxide—had accumulated during the time of initiation. From Fig. 1 it is apparent that in the beginning stages of the reaction (the first 60-80 min at 140°) at similar concentrations of peroxide the rate of the process in the initiated reaction is significantly higher. The experiments in which the process of oxidation was interrupted indicate that a stable product of the interaction of nitrogen dioxide with the hydrocarbon is responsible for the effect of gaseous initiation.

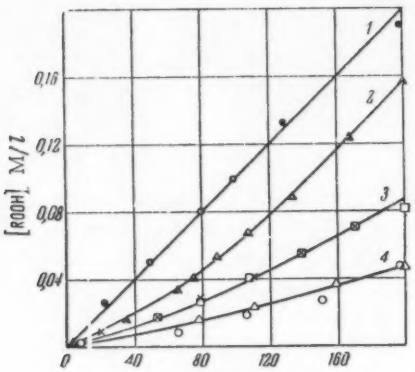

Fig. 4. The decrease of the initiating action of NO_2 as a result of keeping the initiated 2,7-dimethyloctane in an atmosphere of nitrogen at 120° Curves 1, 2 and 3 were obtained in the oxidation by oxygen at 120°. 1) Resting time — 0 min; 2) 80 min; 3) 295 min; 4) uninitiated oxidation.

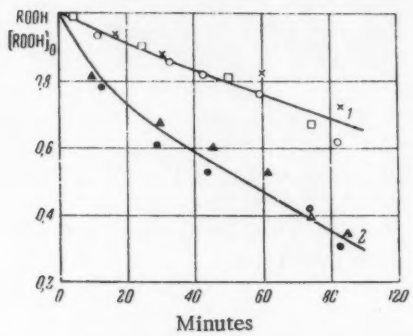

Fig. 5. The kinetics of the decomposition of peroxide in a nitrogen atmosphere at 140°. 1) 14 ml of oxidate + 7 ml of uninitiated 2,5-dimethyloctane; 2) 14 ml of oxidate + + 7 ml of 2,7-dimethyloctane initiated with 10% NO_2 for 5 min. Initial concentration of peroxide — 0.102 M/l.

We made an attempt to decompose the hypothetical initiator, by heating the initiated 2,7-dimethyloctane in a nitrogen atmosphere. After the hydrocarbon was maintained for a certain time in the absence of oxygen at a temperature of 120°, oxygen was introduced into the oxidation vessel. The kinetic curve which was obtained showing the accumulation of peroxide served as a test for the content of the initiator in the system. In proportion to the increase of the time of maintenance in an atmosphere of nitrogen at a high temperature the rate of oxidation was decreased, but even after 5 hr the initiator was not destroyed completely and the rate was greater than in an uninitiated reaction (Fig. 4). These experiments not only confirm the existence of an intermediate initiator, but also demonstrate that in the absence of oxygen it is a relatively stable substance.

The reaction of the intermediate catalyst with peroxide. It was established experimentally that the initiator can react with the peroxide which is formed during the oxidation of the isodecane. In these experiments the kinetics of the disappearance of peroxide in a nitrogen atmosphere were studied. Peroxide was accumulated by means of the oxidation of 2,7-dimethyloctane; after this the vessels were insufflated with nitrogen; into some of the vessels pure hydrocarbon was introduced, and into the remainder 2,7-dimethyloctane previously initiated under standard conditions. In both cases a disappearance of the peroxide was observed (Fig. 5); however in the second case its concentration diminished with much greater rate. Obviously the initiator either reacts with the peroxide or accelerates its decomposition. As far as the initiator itself is concerned its concentration in the hydrocarbon being oxidized must remain constant if it acts as a true catalyst; it must decrease if, on the other hand, it reacts with components of the system.

The weakening of the initiating action of the intermediate substance in the course of the reaction. From Fig. 1 (curves 3 and 4) it is distinctly evident that beginning from some moment the kinetic curves of the initiated and the uninitiated oxidations are parallel. In other words, at the attainment of a certain extent of transformation the reaction as it were "does not remember" what happened in the beginning and develops at the expense of the internal potential – basically due to the branching of the chain at the molecules of peroxide. Two explanations are possible for this phenomena: 1) the initiating action decreases because of the disappearance of the initiator; 2) the initiator does not disappear and maintains its activity, but its initiating action appears small and unnoticeable in comparison with the initiating action of the peroxide which has accumulated by this time in sufficient quantity.

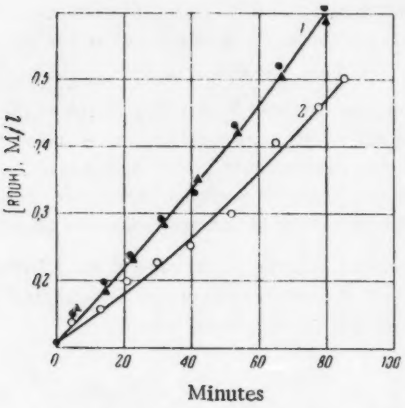

Fig. 6. The kinetics of peroxide accumulation at 140°. 1) 6 ml of oxidate + 3 ml of initiated 2,7-dimethyloctane; 2) 6 ml of oxidate + 3 ml of pure 2,7-dimethyloctane (control experiment). The oxidate was obtained from an uninitiated oxidation of 2,7-dimethyloctane.

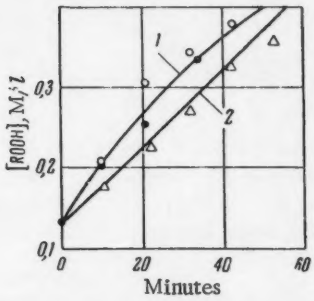

Fig. 7. The kinetics of peroxide accumulation during the oxidation of 2,7-dimethyloctane. The points on the curves correspond to the following mixture compositions. 1) 6 ml of oxidate + 6 ml of initiated isodecane; 2) 6 ml of oxidate + 6 ml of pure 2,7-dimethyloctane (control). The oxidate was obtained from an initiated oxidation of 2,7-dimethyloctane. Curve 2 represents the corresponding (in extent of transformation) portion of the kinetic curve of peroxide accumulation in the standard initiated reaction (for example curve 4 of Fig. 1). The curve falls on the points.

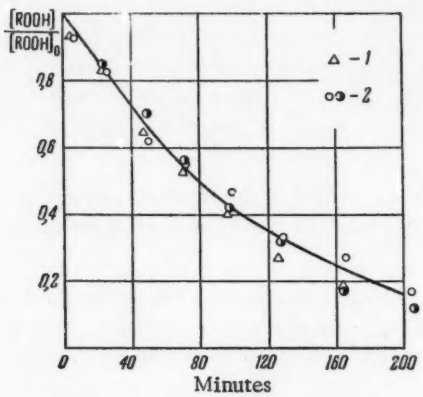

Fig. 8. The decomposition of peroxide obtained by: 1) Oxidation of uninitiated 2,7-dimethyloctane at 140°. $(ROOH)_0$ = = 0.13 M/l ; 2) oxidation of initiated 2,7-dimethyloctane at 140°. $(ROOH)_0$ = = 0.10 M/l .

In the second case, the addition of fresh initiator in an already developed reaction would not lead to an acceleration of the reaction. From Fig. 6, it follows that the addition of initiator at a concentration 1/3 of that at the beginning of the standard experiment to a going reaction causes an acceleration of peroxide accumulation. The increase in the rate of formation of peroxide is even greater then the increase in the rate of its accumulation since the initiator also accelerates the decomposition of the peroxide.

These experiments were repeated, but instead of the oxidate obtained from a noninitiated oxidation oxidate was taken which was obtained by the oxidation of 2,7-dimethyloctane initiated by nitrogen dioxide. If the activity of the initiator does not fall during the course of the oxidation, then the dilution of the oxidate by fresh hydrocarbon initiated by nitrogen dioxide should not change the concentration of the initiator and the rate of accumulation of

peroxide should coincide with the rate in the standard initiated reaction, corresponding to the given extent of reaction (concentration of peroxide).

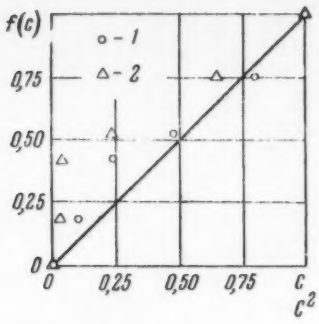

Fig. 9. The dependence of the rate of oxidation of 2,7-dimethyloctane on the dilution of preinitiated hydrocarbon with pure hydrocarbon.

$$f(c)\quad \frac{w_c^2 - \alpha^2 K_0 (\mathrm{ROOH})_c}{w_{1,00}^2 - \alpha^2 K_0 (\mathrm{ROOH})_{1,00}}$$

1 — $f(c)$ in coordinates f, c; 2 — $f(c)$ in coordinates f, c^2

If the activity of the initiator falls then the dilution should increase its concentration and we should have an increase of the rate. From Fig. 7 it follows that there occurs an increase of the rate. Consequently this experiment indicates that there is a decrease of the activity of the initiator in the course of the process.

When the peroxide (obtained by the oxidation of 2,7-dimethyloctane) is decomposed at such concentrations as those at which the accumulation of peroxide in initiated and uninitiated reactions proceeds at the same rate, the kinetics of the decomposition are independent of whether or not the hydrocarbon was initiated at the start of the reaction (Fig. 8).

Consequently, the substance obtained by the interaction of the hydrocarbon with nitrogen dioxide and which is responsible for the acceleration of the reaction disappears during the course of the oxidation reaction; it disappears in the medium of the oxidizing hydrocarbon faster than under conditions such that the oxidation is suspended (in an atmosphere of nitrogen).

The order of the initiating reaction. At the present the following reaction scheme for the oxidation of hydrocarbons is generally accepted for the development of the reaction at a large oxygen pressure.*

$$\mathrm{ROOH} \xrightarrow{K_0} \dot{\mathrm{R}}\mathrm{O} + \dot{\mathrm{O}}\mathrm{H} \qquad (1) \qquad \text{Chain initiation}$$

$$\left.\begin{aligned} \dot{\mathrm{R}} + \mathrm{O}_2 &\xrightarrow{K_2} \dot{\mathrm{R}}\mathrm{O}_2 \qquad (2) \\ \dot{\mathrm{R}}\mathrm{O}_2 + \mathrm{RH} &\xrightarrow{K_3} \mathrm{RO}_2\mathrm{H} + \dot{\mathrm{R}} \qquad (3) \end{aligned}\right\} \text{Chain reaction}$$

$$\dot{\mathrm{R}}\mathrm{O}_2 + \dot{\mathrm{R}}\mathrm{O}_2 \xrightarrow{K_4} \text{Chain termination} \qquad (4)$$

From this scheme the following expression is obtained for the rate of accumulation of peroxide.

$$\frac{d(\mathrm{ROOH})}{dt} = K_3 (\mathrm{RH})\, K_4^{-1/2}\, [K_0 (\mathrm{ROOH})]^{1/2} \qquad (5)$$

or

$$\frac{d(\mathrm{ROOH})}{dt} = \alpha \sqrt{w_i} \qquad (6)$$

where $\alpha = K_3 (\mathrm{RH}) K_4^{-\frac{1}{2}}$ and $\omega_i = K_0 (\mathrm{ROOH})$.

In the presence of the intermediate initiator the scheme for the chain oxidation of hydrocarbons remains unchanged. Only the rate of initiation W_i is changed. It is possible to propose two methods of participation of the intermediate initiator in the initiating reaction:

1. The radicals which initiate the oxidation chains are formed by reaction between the initiator and some product of the oxidation reaction which has accumulated in the system during the time of initiation. Such a substance could be for example a peroxide, which as was shown above reacts with the intermediate indicator I.

$$\mathrm{I} + \mathrm{ROOH} \rightarrow \dot{\mathrm{R}}' + \dot{\mathrm{R}}'' + \text{products}.$$

The rate of initiation in this case is equal to:

$$w_i' = K_{01} (\mathrm{I}) (\mathrm{ROOH}).$$

* Under atmospheric pressure the rate of oxidation of hydrocarbons does not depend on the pressure of oxygen. This indicates that only the peroxidic radicals participate in the chain-breaking reaction.

2. The radicals are formed by the decomposition of the intermediate catalyst itself.

$$I \rightarrow \dot{R}_1' + \dot{R}_1''$$

In this case, for the rate of initiation we have

$$w_i'' = K_{02}(I).$$

In this way in the general case of the oxidation reaction proceeding in the presence of an intermediate initiator the expression for the rate of initiation takes the form

$$w_i = K_0(ROOH) + K_{01}(I)(ROOH) + K_{02}(I). \tag{7}$$

Substituting (7) into (6), we have

$$w = \frac{d(ROOH)}{dt} = \alpha \sqrt{K_0(ROOH) + K_{01}(I)(ROOH) + K_{02}(I)} \tag{8}$$

or

$$w^2 - \alpha^2 K_0(ROOH) = \alpha^2 K_{01}(I)(ROOH) + \alpha^2 K_{02}(I) \tag{9}$$

From expression (9) the order of the initiation reaction in the presence of an intermediate initiator can be determined. The left hand part of expression (9) is known. The value of $\underline{w}$ is determined from the kinetic curves of peroxide accumulation, and the quantity $\alpha^2 K_0(ROOH)$ – from the kinetics of peroxide accumulation in the uninitiated reaction, for which the integrated form of the Eq. (5) is used:

$$\sqrt{(ROOH)_t} = \sqrt{(ROOH)_0} + \frac{\alpha\sqrt{K_0}}{2} t$$

For the determination of the order of the initiating reaction a series of experiments was carried out in which pre-initiated hydrocarbon was diluted with 2,7-dimethyloctane. Each of the diluted portions of the pre-initiated hydrocarbon was oxidized. The initial rate of the oxidation reaction was measured. The dependence of the rate of oxidation on the dilution was obtained in this way. The results of these experiments are presented in Fig. 9. Along the ordinate axis are displayed the ratios of the quantities $w_c^2 - \alpha^2 K_0(ROOH)$, which correspond to the given relative concentration of the initiated hydrocarbon $\underline{c}$ to the quantity $w_{1.00}^2 - \alpha^2 K_0(ROOH)_{1.00}$, which corresponds to the non-diluted initiated hydrocarbon.

From this one ought to expect that

$$f(c) = \frac{w_c^2 - \alpha^2 K_0 (ROOH)_c}{w_{1.00}^2 - \alpha^2 K_0 (ROOH)_{1.00}} = \begin{cases} \dfrac{(I)_c (ROOH)_c}{(I)_{1.00} (ROOH)_{1.00}} = c^2, & \text{if} \quad K_{01}(I)(ROOH) \gg K_{02}(I) \\ \dfrac{(I)_c}{(I)_{1.00}} = c, & \text{if} \quad K_{01}(I)(ROOH) \ll K_{02}(I) \end{cases}$$

i.e., the function $f(c)$ will be expressed by a straight line either in the coordinates (f, c^2) or in the coordinates (f, c) depending on which mechanism of initiation prevails.* As is apparent from Fig. 9, the experimental points satisfactorily lie on a straight line with the coordinates (f, c). In this way $K_{02}(I) \gg K_{01}(I)(ROOH)$ and consequently the initiation of chains occurs basically as a result of the decomposition of the intermediate initiator into radicals.

In this way the principal mechanism of the gaseous initiation in the system investigated consists in the formation of a relatively stable intermediate initiator which accelerates the reaction, decomposing into radicals. This initiator gradually disappears during the course of the process of oxidation but it acts for a long time in comparison with the time of initiation.

The authors express their gratitude to Z. G. Kozlova and N. V. Gerasimova for their help in carrying out the experiments.

* The ratio $(ROOH)_c/(ROOH)_{1.00}$ practically coincides with $\underline{c}$ since the concentration of peroxide in the pre-initiated 2,7-dimethyloctane $[(ROOH)_{1.00}]$ is much greater than $(ROOH)_0$ i.e., than the peroxide which is present as an impurity in the pure hydrocarbon. Instead of ROOH one could substitute the concentration of any other product of the reaction which is formed during the time of initiation and which interacts with the initiator with the formation of radicals.

SUMMARY

1. The brief insufflation of nitrogen dioxide at the beginning of the reaction substantially accelerates the oxidation of 2,7-dimethyloctane by molecular oxygen.

2. As a result of the interaction of nitrogen dioxide with 2,7-dimethyloctane there is formed a relatively stable intermediate initiator.

3. The mechanism of the acceleration consists in the decomposition of the intermediate initiator into radicals which leads to an increase in the rate of initiation.

4. The intermediate initiator gradually disappears during the course of the oxidation but it acts for a long time in comparison with the time of initiation.

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MECHANISM OF THE REACTION OF PLATINUM WITH OXYGEN AT TEMPERATURES UP TO 300°

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On the basis of the concept that any method has some affinity for oxygen, it is possible to obtain an idea of the true surface of a metal. In this report, platinum, far from being an exception, shows general rules particularly clearly.

Information in the literature on the reaction of platinum with oxygen is inadequate and also contains contradictions. As a result of the work of Pauling [1], at one time it was considered that the structure of PtO was known. However, there then appeared papers [2, 3] in which it was stated that this structure was determined incorrectly. Several papers were devoted to the structure of platinum dioxide PtO_2 [4-8], but no accurate conclusions were drawn on the structure (see, for example [9, 10]). The positions of only the platinum atoms were determined accurately in the oxide Pt_3O_4, which was investigated by Galloni and Roffo [11]. As regards the oxygen, our investigations [10] showed that it is present in the structure as the molecular ion so that the formula of the compound actually should be written as Pt_3O_8 or $Pt_3(O_2)_4$. The problem of adsorption of oxygen by platinum at room temperature was found to be more complex and so literature data are even less complete.

The shortcomings of these data were probably caused by an unfortunate choice of subjects for investigation. Different platinum oxides were obtained either from hydroxides or by very prolonged heating of platinum black in oxygen, most often at very high pressures, which yielded mixtures of different products. Sorption phenomena were studied mainly on smooth platinum, which could have had an insufficiently pure surface.

We used different approaches. Platinum condensed in vacuum was used most frequently for investigations. In this way it was found [10, 12] that at normal oxygen pressures, the surface is covered with an oxygen film ~20A thick, which may be evaporated in vacuum. An investigation by volumetric methods showed [13], that the formation of this film occurs very slowly and, within the limits of observations for ten days, obeys a parabolic law, indicating diffusion of platinum ions in the oxygen film. On the basis of electron-diffraction studies, the hypothesis was put forward [10] that oxygen molecules adsorbed by platinum and other metals lie with their long axes normal to the surface. In particular, this followed from a study of a texture diagram of gold peroxide, formed when the metal was heated to 400-500° [14].

EXPERIMENTAL

The following experiments were carried out to obtain new data on the surface compounds of platinum with oxygen. Platinum was condensed on glass plates at a pressure of 10^{-6} mm Hg or somewhat higher. The plates were then heated in a stream of oxygen at different temperatures. It was observed that the nature of the surface compounds of platinum with oxygen depended to a considerable extent on the heating time. The heating time was therefore long enough for the equilibrium state of the products obtained to be approached.

After samples had been heated for 2 hr at 200 and 300°, the oxide crystals had an appreciable texture, but lines of platinum metal were retained to a considerable extent on the electron diffraction patterns and this hampered the investigation. After the samples had been heated for 10 hr, the platinum lines disappeared and the texture diagrams became clearer. As an example we give the electron diffraction pattern in Fig. 1, and the table corresponding to it. When the sample was heated for a further 10 hr, the texture disappeared almost completely, but at the same time there was a change in the structure.

An attempt was made to determine the structure from the electron diffraction pattern in Fig. 1. This was facilitated by the presence on the electron diffraction pattern of three strong short arcs lying on the lines of

symmetry, i.e., at $\delta = 0$, and also other reflections with an integral ratio of the squares of the sines. Our hypotheses on the structure and the axis of the texture are expressed as the results of indexing and as a comparison of the calculated reflection azimuths δ with the observed values (table). In view of the fact that the electron diffraction patterns, obtained with a voltage of 60 kv and a distance from the object to the photographic plate of 250 mm, were very small so that accurate measurements were impossible, the agreement between the experimental and theoretical data may be regarded as satisfactory. Thus, this indexing leads to the conclusion that the lattice in this case is hexagonal with the parameters a = 5.43 A; c = 6.80 A; c/a = 1.25.

Fig. 1. Electron diffraction pattern from a platinum surface heated at 300° in a stream of oxygen.

Further information on the structure could be obtained by the radial distribution method which was used in our previous work [9, 10]. Some data are given in Fig. 2. The solid curve was obtained from mean data from electron diffraction patterns of the given type, including reflections with interplanar distances of 0.434 A. This wide coverage of the series is an excellent guarantee of sharp real maxima. To ensure that the nature of the curve was determined largely by closer reflections, whose positions could be measured with greatest accuracy, the series was stopped at the value d = 0.672 A. The broken curve obtained coincided in the main with the former. The maxima which can be interpreted unequivocally are shaded. The first of them can belong only to the O–O distance in the molecular ion of oxygen. The other three shaded maxima can also be determined unequivocally as belonging to the Pt–Pt distances in the basal plane of the hexagonal cell (Fig. 3). The discrepancy of 0.2 A for the latter maximum is explained by the unfavorable position of the adjacent extrema, which always occurs in this region.

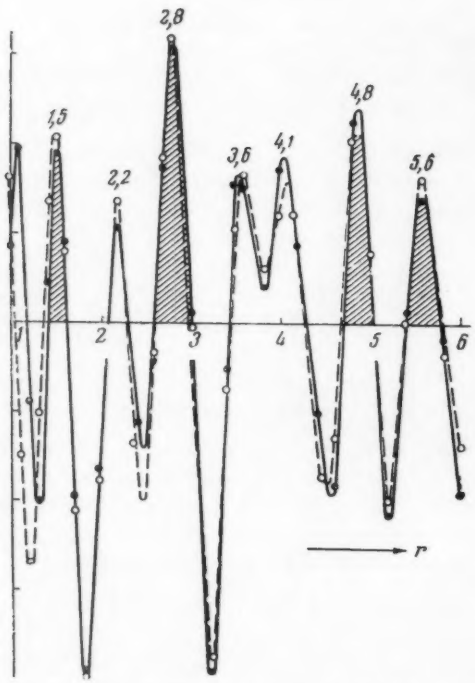

Fig. 2. Radial distribution curve obtained from the mean data from several electron diffraction patterns of the type given.

To explain the origin of the other three maxima it would be desirable to have additional experimental material as intensities measured from texture diagrams may differ considerably from intensities for completely disordered crystals, on which the radial distribution method was calculated. It may be considered that the structure is similar to that of gold peroxide, described previously [14, 10]. This is indicated by the similarity of the lattice parameters in the two cases, the identity of the texture axes, and the presence in the two cases of the molecular oxygen ion, whose size mainly determines the cell dimensions. In this structure the metal ions lie in two layers at a height in the cell of $z = 0$ and at a height of $z = 1/2$. The projection of the structure on the basal plane is illustrated in Fig. 3.

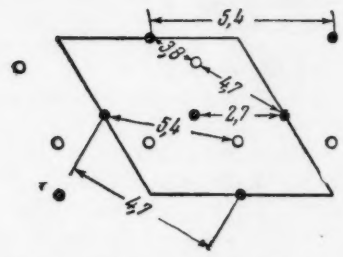

Fig. 3. Projection of hexagonal platinum peroxide on the 001 plane.

Thus, since the plane illustrated is parallel to the metal surface, while the molecular oxygen ions lie with their long axes perpendicular to this plane, it may be considered that the hypothesis put forward previously on this orientation of the oxygen molecules before the formation of the peroxide lattice is again confirmed. This is one of the essential aspects of the problem of the mechanism of the reaction of oxygen with a platinum metal surface.

An attempt was made to demonstrate the orientation of oxygen molecules at room temperature by a direct electron diffraction experiment. Two completely identical glass plates with layers of platinum condensed on them were kept in oxygen at ~0.1 mm Hg for a week after the layer was formed. According to our previous data [10, 13], the surface should have contained a layer of oxygen or oxide of appreciable thickness and about a week would have been required for its complete removal by pumping out. Therefore, in an electron diffraction study where the sample was in vacuum for only half an hour or less before the pattern was photographed, one might have expected a diffraction pattern different from that of pure platinum. The result obtained with one of these plates is given in Fig. 4, which shows that the surface platinum crystals were oriented with the [110] axes normal to the sample surface. The oxygen was undetectable.

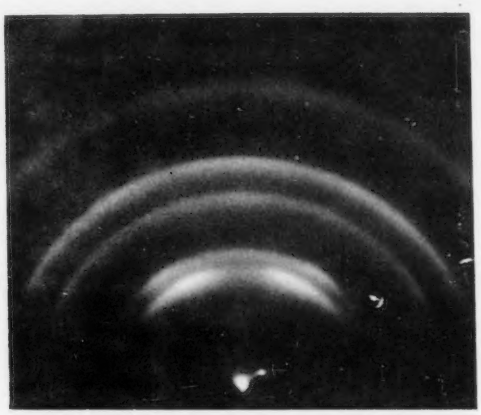

Fig. 4. Electron diffraction pattern from platikept in oxygen for a week at room temperature.

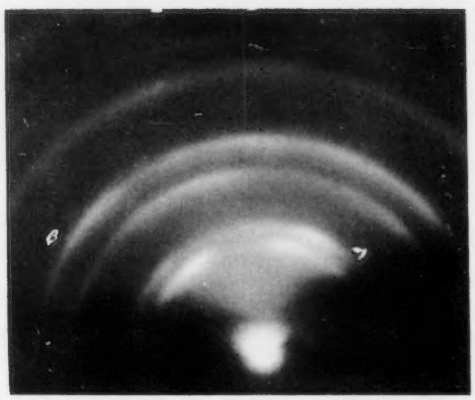

Fig. 5. Electron diffraction pattern from platinum kept in oxygen at 100° for 10 hr.

The second plate was heated at 100° in a stream of oxygen for 10 hr before the electron diffraction patterns were photographed. The electron diffraction pattern obtained after this (Fig. 5) shows that the texture axis remained the same, but was inclined to the normal to the sample surface. It might be considered that the change in orientation occurred under the influence of oxygen adsorbed on the platinum surface at 100°. However, it is difficult to visualize all the crystals or even some of them simultaneously undergoing this rotation under such conditions.

It seems more natural to assume that normal recrystallization occurred, but under the influence of the surface oxygen layer, which weakens the bonds of the surface platinum atoms with the remaining mass of the metal and also compels the moving atoms to fit in with the structure of the oxygen layer itself. In this case there is the possibility

that the first orientation at room temperature (see Fig. 4) occurred not during the condensation of the platinum atoms, but subsequently under the influence of the oxygen layer, which exists at room temperature.

Results of Processing Electron Diffraction Patterns from Platinum Heated at 300° in a Stream of Oxygen for 10 hr

Intensity, I	Reflection azimuths, δ	Interplanar distances, d	Indices, hkl	Theoretical data	
				δ	d
3	50°	3,82	101	60°	3.87
10	0°	3,40	002	0°	3,40
10	50°	2,75	110 102	90° 40°	2,72 2,76
1	50°	2,55	111	70°	2,52
2	80°	2,35	200	90°	2,35
3	40°	2,04	103	30°	2,04
2	50°	1,94	202	60°	1,93
4	0°	1,72	004	0°	1,70
2	Line	1,63	203 104		1,63 1,60
3	70°	1,55	300 212	90° 55°	1,57 1,57
1	45°	1,46	114	30°	1,44
2	70°	1,36	220 221	90° 80°	1,36 1,33
2	0°	1,33	105	15°	1,31
1	70°	1,28	310 311 303	90° 80° 60°	1,30 1,28 1,29
1	80°	1,20	400	90°	1,18
1	Line	1,16	401 223	90° 30°	1,16 1,16
3	0°	1,12	006	0°	1,13

In conclusion, we should note that this view is contrary to the wide-spread opinion that the oxygen adapts itself to the metal surface structure and the latter predetermines the structure and orientation of the oxide formed later. On the contrary, in our opinion the oxygen layer acquires an independent structure, which is subsequently the basis structure of peroxides formed later, while atoms of the surface layers of the metal adapt themselves to the existing structure of the oxygen.

SUMMARY

1. The products from the reaction of platinum with oxygen at moderate temperatures are various platinum peroxides.

2. Even on a pure platinum surface, oxygen is chemisorbed without decomposition of the molecules to atoms.

3. In the formation of a peroxide film there are considerable changes in the structure of the surface of the metal itself, which shows, in particular, in a change in the orientation of its crystals.

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HOMOGENEOUS CATALYSIS IN GAS-PHASE OXIDATION OF HYDROCARBONS

COMMUNICATION 2. EFFECT OF NITROMETHANE ON THE OXIDATION OF METHANE

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In a previous communication [1] it was shown that the two heat evolution maxima during the oxidation of methane in the presence of small amounts of NO_2 are connected with the reaction of methane with NO_2 and subsequent catalytic oxidation of methane. The oxidation of methane under the same conditions, but without NO_2 added, proceeds extremely slowly with an induction period of ~20 min, while the reaction catalyzed by nitrogen dioxide is practically complete in a few minutes. The investigations showed that the vigorous reaction of NO_2 with methane forms the intermediate product nitromethane, which then catalyzes the oxidation of methane. This does not mean that NO_2 itself cannot generate active reaction centers. The most probable mechanism of the catalytic action of nitromethane is the initial binding of the NO_2 and then slow decomposition with the liberation of NO_2, which readily generates active centers.

In the present work we investigated the effect of nitromethane on the kinetics of methane oxidation and the behavior of the nitromethane itself in the complex oxidation process. The basic plan of the experimental apparatus, the reaction vessel, and the investigation procedure were described in the previous communication. In the same work it was shown that the addition of nitromethane leads to the appearance of only the second heat evolution maximum, which is connected with methane oxidation, while the addition of NO_2 produces two heat evolution maxima: the first is connected with the reaction of methane with NO_2, in which nitromethane is formed, and the second is connected with methane oxidation. If these ideas are correct, one would expect that under otherwise equal conditions, a reaction mixture containing nitromethane would react at a higher rate than a mixture containing the same amount of NO_2, as in the latter case, the catalytic oxidation is preceded by the reaction of NO_2 with methane, as a result of which nitromethane is formed in smaller amounts than the amounts present in the first mixture.

Figure 1 shows kinetic curves of methane and oxygen consumption and the accumulation of H_2O, CO, and CO_2 for the mixture $CH_4 + 2O_2 + 2\%\ NO_2$; analogous curves for the mixture $CH_4 + 2O_2 + 2\%\ CH_3NO_2$ are given in Fig. 2. As Figs. 1 and 2 show, the kinetic curves are largely similar with the difference that in mixtures containing nitromethane, the reaction proceeds to a greater extent both with respect to oxygen comsumption and the accumulation of CO_2 and H_2O.

The rates of methane and oxygen consumption for reactions with NO_2 and CH_3NO_2 added are compared in Fig. 3. The reaction rates are practically the same in the two cases. At first glance, this fact seems to contradict our hypotheses, according to which the reaction rate should be higher with CH_3NO_2 added than with NO_2 added. However, as Fig. 4 shows, the stationary concentration of CH_3NO_2 when nitromethane is added and its maximum concentration when NO_2 is added are of approximately the same order. This eliminates the apparent contradiction in our arguments, but hampers the solution of the main problem, namely, whether nitromethane or NO_2 is the catalyst. The observed identical reaction rates for mixtures with practically equal amounts of nitromethane would solve the problem in favor of catalysis by nitromethane were it not for the fact that the amounts of NO_2 in the two cases might also be the same. Therefore, it is impossible to draw an unequivocal conclusion on the basis of these data. On comparing the kinetic curves of nitromethane consumption with the heat evolution in the case of methane oxidation catalyzed by CH_3NO_2, one is struck by the fact that the time at which the second maximum is reached coincides accurately with the time when there is a sharp fall in the concentration of CH_3NO_2 in the system (Fig. 5). In addition, Figs. 1 and 2 show that practically all oxidation stops at this moment.

On the basis of these experimental data it may be considered that the catalysis in all probability is effected by the nitromethane as methane oxidation stops when the nitromethane is exhausted. However, first, the methane and oxygen have been consumed to a considerable extent by the time the nitromethane in the system is exhausted and the halt in the process may be caused by the lack of starting materials and secondly, it is possible that the formation of the second maximum may lead to complete exhaustion of the nitromethane, promoting the conversion of NO_2 to NO or some other form, and consequently the halt may be explained by the absence of NO_2 from the system. To determine whether the sharp fall in the CH_3NO_2 concentration is connected with the methane oxidation process or the peculiarities of CH_3NO_2 oxidation, we carried out experiments on the kinetics of nitromethane decomposition in an atmosphere of oxygen, nitrogen, and methane.

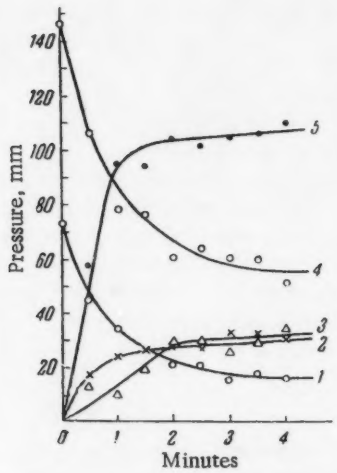

Fig. 1. Kinetic curves of the consumption of starting materials and the accumulation of intermediate and final products in the mixture $CH_4 + 2O_2 + 2\%\ NO_2$; T = 473°; p = 225 mm. 1) CH_4; 2) CO; 3) CO_2; 4) O_2; 5) H_2O.

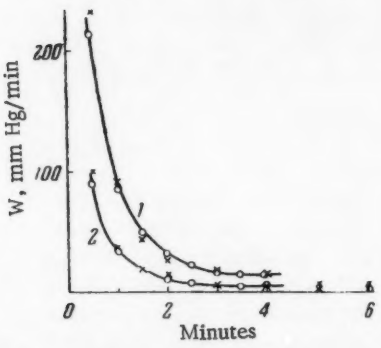

Fig. 3. Rate of consumption of methane (2) and oxygen (1) in the systems $CH_4 + 2O_2 + 2\%\ NO_2$ (0) and $CH_4 + 2O_2 + 2\%\ CH_3NO_2$ (x).

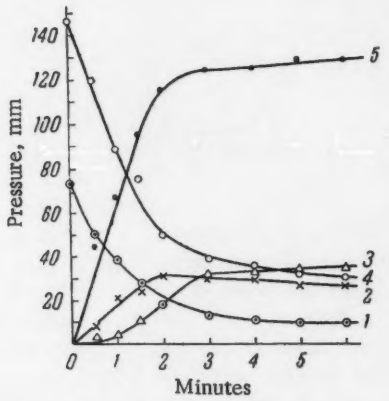

Fig. 2. Kinetic curves of the consumption of starting materials and the accumulation of intermediate and final products in the mixture $CH_4 + 2H_2O + 2\%$ CH_3NO_2; T = 473°; p = 225 mm; the symbols on the curves are the same as in Fig. 1.

Figure 6 gives kinetic curves of the decomposition of 4.7 mm of nitromethane at 473° and a total pressure in the system of 225 mm in the given media. As the kinetic curves show, the lowest rate of nitromethane decomposition was observed in a medium of methane being oxidized. The decomposition rates were approximately the same in N_2, O_2, and CH_4. In the oxidizing medium, the nitromethane was first consumed to a definite concentration (approximately a half under our conditions) and then its concentration remained constant up to the second heat evolution maximum. This phenomenon may be explained in two ways: either the decomposition of nitromethane is a chain process and the other chain reaction occurring simultaneously, namely, methane oxidation, inhibits this process or during the reaction, nitromethane is simultaneously consumed and formed from methane during the oxidation reaction. The latter is more probable.

To solve this problem, we made a special study with labeled methane and nitromethane, whose results will be given in the next communication. No less important is the coincidence in time of the second maximum and the

sharp fall in nitromethane concentration on the kinetic curve. This phenomenon is apparently explained by the fact that at this moment there is chain self-ignition of the carbon monoxide formed by oxidation of methane. In many experiments with high concentrations of NO_2 or CH_3NO_2, at the moment of the second maximum we observed quite a bright flame, accompanied by a jump of the scale spot of the membrane manometer and the mirror galvanometer measuring the heat evolution of the reaction. With a decrease in the NO_2 or CH_3NO_2 concentration, the color of the flame changed from yellow to blue and disappeared altogether, though the heat evolution was recorded by the instrument. If the second maximum is connected with chain self-ignition of carbon monoxide, then the addition of CO to the starting mixture should reduce the time before the second maximum appears. As Fig. 7 shows, the time before the second maximum appears decreases with an increase in the CO concentration. According to our ideas, during the combustion of the CO, regardless of its intensity, there is a sharp increase in the concentration of O atoms, which, in addition to methane, CO, etc., attack and decompose nitromethane. To check this hypothesis, we carried out the following experiments. To mixtures of 4.7 mm of CH_3NO_2 (the amount we normally used in our experiments) and 220.3 mm of O_2 (total pressure 225 mm) were added increasing amounts of carbon monoxide and the nitromethane concentration determined after the mixtures had remained in the reaction vessel for 30 sec. The results are shown in Fig. 8. At first, an increase in the CO concentration had no effect on the CH_3NO_2 concentration remaining after 30 sec. Beginning with a definite critical CO concentration (p_{cr} = 15 mm in our case), the CH_3NO_2 concentration fell sharply.

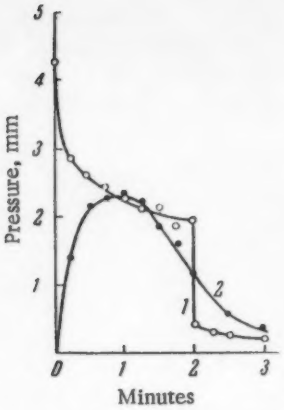

Fig. 4. Relation of nitromethane consumption to time in the mixture $CH_4 + 2O_2$ with 2% of nitromethane added at T = 473°; p = 225 mm (1) and the relation of nitromethane accumulation to time in the mixture $CH_4 + 2O_2$ with 2% of NO_2 added at T = 473° and p = 225 mm (2).

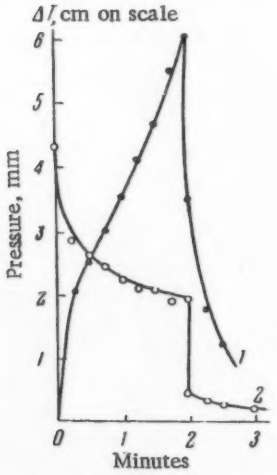

Fig. 5. Relation of the change in heat evolution to time for the mixture $CH_4 + 2O_2 + 2\%$ CH_3NO_2 at T = 473° and p = 225 mm (1) and the change in nitromethane concentration in the same system (2).

As we explain the decrease in nitromethane concentration by chain combustion of CO, the curves of CO and CO_2 accumulation and O_2 consumption should show some change at the point where chain combustion of CO occurs. However, this was not observed and its absence may be explained only by a slight burn out of the CO. As soon as combustion occurs and part of the CO is consumed, the system returns to the state preceding combustion and consequently there cannot be much combustion of CO. The CH_3NO_2 concentration then becomes lower and lower.

At high concentrations, the ignition of CO was visible to the eye, but could not be observed with a decrease in concentration. Thus, these data show that with chain combustion of carbon monoxide, the nitromethane concentration in the system decreases sharply. The detailed mechanism of this process is difficult to establish at the present time, but the very fact that chain combustion of carbon monoxide affects the kinetics of CH_3NO_2 consumption is in good agreement with concepts of branched chain reactions.

It is important to determine why there is no appreciable sharp change on the kinetic curves of CO and CO_2 accumulation and oxygen consumption with chain combustion of the carbon monoxide accumulating during methane oxidation. This is apparently explained by the fact that with the accumulation of carbon monoxide, which was not present at the beginning of the process, the system gradually passes to a state where chain combustion of CO is possible, i.e., approaches a limit. As soon as combustion occurs and part of the CO is consumed, the system returns to the state preceding combustion, i.e., penetration deep into the combustion peninsula is impossible and, consequently, not much CO can be consumed.

As Fig. 8, shows in our experiments the critical CO concentration equaled 15 mm, while in the oxidation reaction the second maximum appeared when 35-40 mm of CO had accumulated, as Fig. 2 shows. This apparent contradiction is explained by the fact that chain self-ignition of CO is strongly

inhibited by hydrocarbons and, in particular, methane. The effect of methane on the ignition limits of carbon monoxide and hydrogen has been studied thoroughly [2-3]. If the increase in the critical concentration of carbon monoxide is connected with the presence of methane in the system, with a decrease in the methane concentration, this critical CO concentration should fall and, consequently, the time to reach the second maximum should decrease.

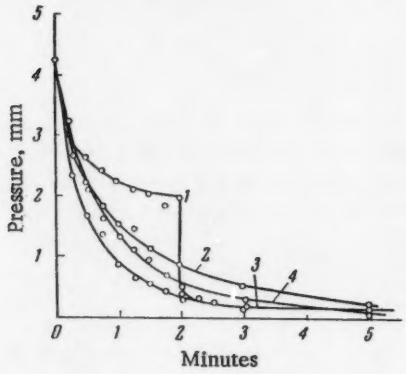

Fig. 6. Relation of nitromethane concentration to time at p = 225 mm, CH_3NO_2 – 2%, and T = 473° in the medium: 1) CH_4 + $+2O_2$; 2) nitrogen; 3) oxygen; 4) methane.

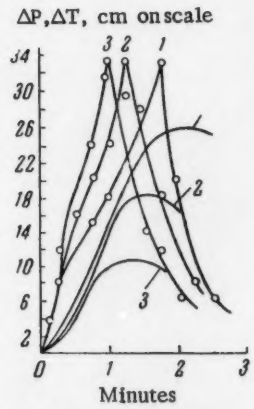

Fig. 7. Effect of CO on the time before the second maximum appears. Changes in heat evolution and pressure in the system with and without additives at T = 473° and p = 225 mm: 1) without additives; 2) with 10% CO added; 3) with 20% CO added.

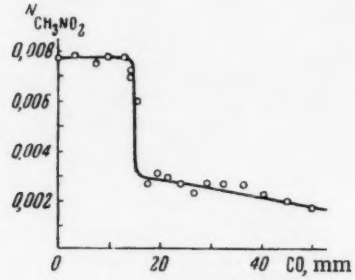

Fig. 8. Change in CH_3NO_2 concentration in relation to CO content of mixture at p = 225 mm and T = 473 mm; CH_3NO_2 – 4.7 mm; p = 220.3 mm.

To check these hypotheses, we carried out the following experiments. Part of the methane in the mixture of methane, oxygen, and nitromethane was replaced by nitrogen. As Fig. 9 shows, the time for the second maximum to appear decreased with decrease in the methane concentration, indicating that the critical carbon monoxide concentration necessary for ignition falls with a decrease in the methane concentration. The combination of facts presented above shows that the appearance of the heat evolution maximum with the subsequent halt in the oxidation reaction is connected with chain self-ignition of carbon monoxide.

On the basis of the experimental data obtained it is impossible to draw an unequivocal conclusion on the nature of the acceleration of methane oxidation. NO_2, NO, and CH_3NO_2 are present in the system simultaneously. It may be considered that the generation of active centers proceeds by the reaction:

$$CH_4 + NO_2 \rightarrow CH_3 + HNO_2 \qquad (1)$$

However, as was shown in the previous communication, the reaction of NO_2 with methane under these conditions proceeds in 15-30 sec, while the oxidation continues for several minutes. On the other hand, it is evident that the life of one chain under these conditions does not exceed a fraction of a second. Therefore, if it is considered that the generation process occurs by scheme (1), then it must be assumed that the reaction of NO_2 with methane forms some comparatively stable intermediate substance, which then decomposes slowly, supplying NO_2 to the mixture.

This intermediate substance may be nitromethane, which is the most stable intermediate under these conditions. However, nitromethane itself may generate active centers by the reaction

$$CH_3NO_2 \rightarrow CH_3 + NO_2 \qquad (2)$$

The experimental data obtained does not give adequate ground as yet for stating that generation proceeds according to scheme (1) or (2). This will be elucidated by further investigation.

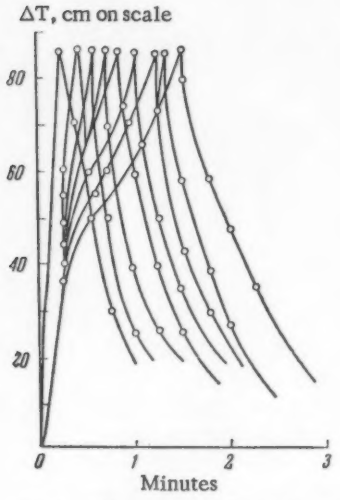

Fig. 9. Effect of a decrease in CH_4 concentration on the time to reach the second maximum in the mixture $CH_4 + 2O_2 + 2\% CH_4NO_2$ at T = 473° and p = 225 mm.

SUMMARY

1. An investigation was made of the kinetics of methane and oxygen consumption and the kinetics of accumulation of the final reaction products in mixtures containing NO_2 and CH_3NO_2 and it was shown that the oxidation rates are approximately the same in the two cases.

2. The appearance of a second heat evolution maximum with a subsequent halt in the oxidation is connected with chain self-ignition of carbon monoxide.

3. In a medium of methane being oxidized, the apparent decomposition rate of nitromethane is less than in O_2, CH_4, and N_2.

4. The nitromethane concentration falls sharply with chain self-ignition of carbon monoxide.

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CONTROLLING FACTORS IN THE PROTECTION OF METALS FROM CORROSION

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Great interest is attached to the development of existing methods for the prevention of corrosion of metals, starting from the inhibition of the basic step of electrochemical corrosion. Apart from providing the most rational scientific classification of the possible methods of anti-corrosive protection, such an approach might indicate the best conditions for using each method and their most effective combinations.

There exist a very large number of different methods for preventing corrosion. These methods are so various in character that it appears impossible to see in them any general factor, such as is necessary for a rational classification based on a single scientific system. Let us recall the basic methods which are widely used to protect metallic structures from corrosion, and arrange them firstly, as is generally done, according to the different ways in which they are carried out: 1. Protective coatings. Organic coatings (paints, high-polymers, greases). Inorganic coatings (oxides, phosphates, chromates, etc.). Metallic coatings of various types (metallization, sublimes, diffusion, plated). The protective coatings can differ very much in their thicknesses, starting from very thin protective layers like the adsorbed passive films (tens of angstroms), up to thick linings (refractories) constructed from protective materials, the layers of which are some 2-3 cm thick. 2. Treatment of the corroding medium to reduce its corrosive activity. As examples one can cite neutralization and deoxygenation of liquid media, the use of different types of inhibitor, especially volatile ones, which have been widely used to protect metallic parts in atmospheric conditions, and some others. 3. Electrochemical protection based on the methods: a) cathodic protection and the use of protectors; b) anodic electrochemical protection; c) protection from stray currents by use of electrodrainage. 4) Development and use of new metallic constructional materials with increased corrosion stability. 5. Rational construction and exploitation of metallic installations and parts.

From the scientific point of view it is more interesting to analyze and classify the various methods enumerated not on the basis of their conditions of use or the technology of their application, but by the application of the electrochemical theory of corrosion and discussion of the mechanism of the protective effect of each method. It is possible to carry out such a classification, but it is essential to establish correctly for each protective method the stage of the corrosion process which is retarded by the given protection method i.e., to establish the basic controlling factors of the particular protective method.

It appeared that one could choose with sufficient certainty for each method of corrosion protection the step of the corrosion process whose deceleration determines the general reduction in rate of the corrosion process. It is known [7, 9] that the dependence of the corrosion current (which characterizes the rate of corrosion) on the basic factors of electrochemical corrosion is defined by the equation:

$$I = \frac{V_к^\circ - V_a^\circ}{P_к + P_a + R}$$

where $V_k^0 - V_a^0$ is the difference between the initial equilibrium potentials of the cathodic depolarization process (V_k^0) and the anodic reaction of the dissolved metal (V_a^0). These values, which are equal to the EMF of the corrosion element, will be proportional to the decrease in free energy of the system when the corrosion process occurs. The value $V_k^0 - V_a^0$ can be regarded as the degree of thermodynamic instability of the system. The denominator of the expression given will represent the more general inhibition of the system; in the formula it is expressed by three

terms with ohmic dimensions; the mean cathodic and anodic polarizabilities (P_k and P_a) and the general ohmic resistance of the system (R).

Consequently the strength of the corrosion current (I) will, in the general case, depend on at least four factors; 1) the degree of thermodynamic instability of the system ($V_k^0 - V_a^0$); 2) the mean cathodic polarizability (P_k); 3) the mean anodic polarizability (P_a); 4) ohmic resistance of the corrosive elements. These four factors rationally form the basis for a scientific classification of the different means for decreasing the rate of corrosion.*

For metals, decrease in corrosion is connected with inhibition of the cathodic process. Hence, for example, the use of cathodic inhibitors which increase the over-potential of the cathodic depolarization reaction, the decrease in the concentration of cathodic depolarizers in solution, e.g., hydrogen ions or dissolved oxygen, the decrease in active cathodic inclusions in the alloy, and some other things. To cathodic inhibition also belong the widely used methods of cathodic electrochemical protection, especially the use of protectors. The fact that cathodic electrochemical protection belongs to the methods which inhibit the cathodic process follows directly from the simple definition of the type of control.

As has been described previously [7-9] quantitative determination of the control can be carried out starting from the known value of the corrosion potentials (V_x) and the initial potentials of the cathodic (V_k^0) and anodic (V_a^0) processes. In particular the extent of cathodic control (C_k) will be determined by an expression:

$$C_к = \frac{V_к^0 - V_x}{V_к^0 - V_a^0} \cdot 100$$

It is obvious that with constant values for V_k^0 and V_a^0 any decrease in the value of V_x, i.e., a shift of the corrosion potential (V_x) in the negative direction, will correspond to an increased degree of cathodic control. Thus, cathodic protection, which is connected with a shift of the potential of the corroding surface (V_x) in the negative direction, can be interpreted as a decrease in corrosion due to an increased degree of cathodic control of the corrosion system. The mechanism of the principal inhibition of cathodic processes using cathodic electrochemical protection or the use of protectors can be understood thus: When the corroding surface is polarized cathodically with a surface current the microcathodes are so energetically overloaded from the surface circuit with its more energetic anode that they cease to work in the internal circuit because the corroding surface is a less active anode than the applied protector, for example.

Many methods of protection are based on inhibition of the anode process, for example: introduction of anodic inhibitors or general "passivating" reagents into the solution; increasing the ability of metal to be rendered passive by alloying it, and also special additions of noble metal ions to the solution, or introduction of noble metals into the metal structure. To anodic inhibition also belongs the recently discovered form of corrosion prevention with anodic electrochemical protection which may be carried out when the metal easily undergoes anodic passivation in the given conditions [10-14].

The possibilities of methods of protection against electrochemical protection based on increased ohmic inhibition are more limited. This is connected with the decreased role of ohmic control on electrochemical corrosion processes, especially in those cases in which the corrosion process is determined by the work of a micro- or submicro-cell [14]. However, for example, the method of protection against subterranean corrosion (which arises as a result of the effects of macroscopic cells) by drainage of the soil around the subterranean structure should certainly be placed in this category.

Many methods of protection against corrosion should be connected with lowering the degree of thermodynamic instability of the given corrosion system. The degree of thermodynamic instability of the system is determined not only by the character of the metal itself but also by the surrounding corrosion medium and the general physical properties of the system under discussion. Covering a thermodynamically active metal with a compact layer of a thermodynamically more stable metal (e.g., covering copper or copper-steel with gold, or steel with nickel) and also alloying the metal with a sufficiently large quantity of a more stable component (e.g., nickel with copper, or chrome steel with nickel) are examples of combating corrosion by lowering the degree of thermodynamic stability of the system.

* Analogous ideas are used not only to analyze the inhibition of electrochemical corrosion of metals but also to analyzethe more general case of the course of electrochemical heterogeneous reactions.

One cannot always decide immediately where to place methods which decrease the concentration of cathodic and anodic depolarizers which simultaneously affect not only the cathodic and anodic polarizability but also the initial cathode and anode potentials (V_k^0 and V_a^0). For example a reduction in the content of oxygen in the corrosion medium can be discussed either as cathodic inhibition or as a reduction in the thermodynamic instability of the system. A qualitative decision on this question can be obtained by determining the character of the change in value of the cathodic control (C_k) with changing conditions of corrosion. It is evident that it can be thought, approximately, that an initial decrease of the oxygen concentration in the solution can be described as cathodic deceleration. Complete exclusion of oxygen from the system by complete isolation of the metallic surface should be discussed as a decrease in corrosion as a result of decreased thermodynamic instability of the system.

Starting from these considerations, non-swelling (non-electrolytic) isolating organic and inorganic coatings, and also vitreous enamels and refractories, should be discussed as methods which increase the thermodynamic stability of the system. If the covering is not compact but porous then this statement applies only to the part of the metal surface which is not in contact with the corrosive medium. On the other hand paint coatings which swell (considerably with ions) are more rationally placed among protective methods which increase cathodic, anodic, or ohmic control. A more exact classification of the coating by the mechanism of its action is possible only after a more detailed study of the mechanism of its decelerating action on the corrosion process and a quantitative determination of the controlling factors for each type of coating. In those cases in which a quantitative study of the mechanism of the protective effect of the coating has not yet been made, we shall attribute their action to isolation of the metal from the corrosion medium i.e., to increased thermodynamic stability of the system.

A similar classification of protective measures according to their mechanism of decelerating electrochemical corrosion is given in the Table. As a basis of this classification we use the type of effect of the given form of protection on either the driving force of corrosion (change in the degree of thermodynamic instability) or the basic controlling factors of corrosion. In agreement with conclusions of the electrochemical theory of corrosion all the known and possible methods of anticorrosive protection should be distributed into four main groups according to the type of their effect on the corrosion process: 1) methods which decrease the degree of thermodynamic instability of the corrosion system; 2) methods which decrease the rate of corrosion by decelerating the cathode process (increased cathodic control); 3) methods which basically decelerate the anode process (increased anodic control); 4) methods which decelerate the corrosion process by ohmic factors (increased ohmic control).

To decrease the complexity we shall not specify the dependence of the thermodynamic instability of the character of the deceleration of the corrosion process on more elementary steps which can be introduced if necessary. Within each of these groups we have introduced three further sub-groups based on whether the method under discussion worked by changing internal factors which depend on the metal (e.g., change in composition or structure of the metal); or which depend on changing the surface of the metallic object (e.g., carrying out some treatment on the metal surface or applying some sort of protective coating); or which changes the surrounding conditions and the character of the corrosion medium, i.e., depends principally on the external corrosion factors.

It is evident that all known and possible methods of protection can find a place in the Table, agreeing with the character of the driving force or decelerating (controlling) effect of each type of protection.

The introduction of proper systematization permits one to use the known methods of protection most completely and correctly. It makes possible the selection of the rational direction of further study in the development of new protective methods. We shall cite some examples.

If the basic controlling factor of a given protective method is known then one can indicate in which conditions its use will be most effective, and which factors will strengthen it and which weaken it. For example the urge to decrease the rate of metallic corrosion by increasing its purity and possibly decreasing cathodic impurities is a suitable method of countering corrosion in conditions where the basic controlling factor of corrosion is the overloading of the cathodic depolarization process. According to this principle the use of this method of countering corrosion would be effective against the solution of metals in acidic media (e.g., corrosion with hydrogen depolarization). According to this principle the purest metals (such as zinc, aluminium, magnesium, and a series of others) which do not contain cathodic impurities with a lower overpotential of hydrogen than the principal metal, will dissolve in dilute acids (aluminium and magnesium also dissolve in neutral chlorides) far more slowly than the same metals loaded with cathodic impurities. On the other hand, in different conditions such as corrosion with oxygen depolarization (when the basic controlling factor is most frequently the diffusion of oxygen), a possible in-

crease in purity of the metal would not give a positive effect, and in cases of corrosion with anodic control increased purity of the metal might be not only useless but even harmful. In a series of investigations carried out recently [10, 12] it was shown that in conditions in which a passive state could arise (i.e., corrosion conditions characterized by an initial high anodic control) a metal containing cathodic inclusions more easily passed into the passive state.

Decrease of the concentration of oxygen or oxidant in the solution, which is an excellent method of protection in conditions of corrosion with cathodic control (e.g., corrosion of iron in chloride solutions or in sea water) would be not only useless but even harmful if the corrosion process was determined to a considerable extent by anodic control, as in using stainless steel in these electrolytes. In the last case a decreased rate of aeration leads not to a decrease, but to an increase, in the rate of corrosion. Alloying the steel with a large quantity of chromium (transition to chrome steel) is a perfect method of protection in conditions providing a stable passive state (anodic control) but it would be completely useless for construction work in non-oxidizing acids (HCl, H_2SO_4) in which corrosion is under cathodic control.

One can also introduce a more general correctness into the choice of a suitable method of protection. It is most likely in the general case that the most easily carried out method of protection will be that which retards the basic controlling factor of the corrosion process under discussion i.e., the method in which the controlling factor for protection coincides with the controlling factor for corrosion. This does not mean that protective methods with different controlling factors (in principle) cannot be used. For example even in a "passivating system" in which corrosion is based on anodic control, one can achieve corrosion protection by total prevention of the cathode process, e.g., by intense cathodic polarization, although initially when the cathodic current density is least even a slight increase in corrosion may occur. However as a general conclusion it should be noted that if the protective method used gives only partial retardation of a particular corrosion stage, then it will be easy to attain a more effective retardation of the corrosion process if a protective method is chosen which affects the basic controlling factor for corrosion.

If several methods of protection are used in parallel then, as a rule, it is easier to attain the most complete protection if all the methods used preferentially affect the basic controlling factors of corrosion. For example, when corrosion of metals in acid has been decreased by increasing the purity of the metals, the simultaneous use of protective methods affecting other factors which retard cathodic processes would also help (e.g., introduction of cathodic inhibitors in the solution, increased pH of the medium, etc.).

When corrosion is limited by superimposition of a passive state, e.g., by introduction of "passivating" agents, a parallel strengthening of the protective effect can be obtained by the introduction of cathodic covering, or anodic polarizers, i.e., a series of metals which affect by retardation only the anodic processes. On the other hand, simultaneous use of some methods with different controlling factors will be less effective as a rule, and may even be deleterious, because the methods with different controlling factors may interfere with one another. For example if corrosion is restricted by methods which retard the anodic process (alloying steel with chromium, addition of oxidizers or anodic inhibitors to the solution), then it is not rational to try to use at the same time methods which retard the cathodic process (elimination of cathodic inclusions from the alloy, decreased aeration of the solution, or addition of cathodic inhibitors to the system).

On the other hand the use of protective methods, which reduce the degree of thermodynamic instability of the system, will always make possible a reduction of the rate of corrosion independently of the basic control of the corrosion system and of the controlling factors of the other protective methods used at the same time. However, in general, with a large total retardation ($P_k + P_a + R$ very large) the system will be more inert with regard to the possibility of changing the rate of corrosion by changing the degree of the thermodynamic instability.

The development of the classification of different protective methods which is cited in the Table is the first attempt to get systematization of protective methods according to the type of their effect on retardation of the basic steps of the electrochemical corrosion process and the degree of thermodynamic instability. Undoubtedly in the future with the use of more widespread data on the quantitative nature of the influence of each type of protection on the electrochemical corrosion process, this classification may be made considerably more exact. But even in its qualitative form the systemarization introduced can be useful for the correct understanding of the possibilities and peculiarities of each protective method and for the most rational use of this or that protective method in the given conditions.

Rational Classification, Based on Electrochemical Theory, of the Possible Methods of Combating Metallic Corrosion

Change in the accelerating or retarding factors of the corrosion process	General character of the preventive measures	Concrete examples of anticorrosive protections	Practical examples of the protective method
1	2	3	4
Decrease in the degree of thermodynamic instability of the system.	Change in internal factors (of the metal).	1. Alloying, which increases the thermal stability of the alloy.	1. Alloying copper with gold, nickel with copper, and chrome steel with nickel.
		2. Additions to the metal which make possible a more compact form of the corrosion products.	2. Introduction of copper into low-alloy steel during atmospheric corrosion (increased compactness of the rust on copper steel).
	Change in factors of the surface of the article.	1. Covering the article with a compact layer of a more noble metal.	1. Plating iron with copper or nickel.
		2. Isolation and paint coverings.	2-6. There are many practical recipes using the corresponding protective coverings.
		3. Oils.	
		4. Linings and coverings of non-metallic materials.	
		5. Oxides, phosphates and other layers.	
		6. Enamelling.	
		7. Coverings of metals which form more protective layers of corrosion products.	7. Covering iron with zinc for use in the atmosphere or fresh water (formation of more protective corrosion products on Zn).
	Change in surrounding factors (surrounding conditions or medium).	1. Change in the surrounding medium to make possible the formation of more protective (isolating) layers on the surface of the article.	1. Removal of free carbon dioxide from water and shifting the equilibrium of the reaction $CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca(HCO_3)_2$ towards the formation of $CaCO_3$ (to the left). Use of inhibitors with isolating properties (phosphates, etc).
		2. Change in the corrosion conditions to make possible the formation of more protective layers on the surface.	2. Secondary effects of cathodic protection under maritime conditions (formation of carbonate protective layers).
		3. Change in the corrosion conditions to eliminate or radically decrease the access of corrosive materials to the metal surface.	3. Elimination of complex-forming reagents from the solution or increase in the concentration of proper ions of metals in solution (corrosion of Zn and Cu). Elimination of cathodic depolarizers (H^+, O_2, and other oxidants) from solution. Storage of the articles in special containers in an inert or vigorously dried atmosphere (use of silica gel, alumina gel, and other desiccants, against atmospheric corrosion.

TABLE (continued)

Change in the accelerating or retarding factors of the corrosion process	General character of the preventive measures	Concrete examples of anticorrosive protections	Practical examples of the protective method
1	2	3	4
			Use of protective atmospheres (N_2, Ar, etc.,) to eliminate electrochemical and also chemical high temperature corrosion.
Increase in cathodic control.	Change in internal factors (metal).	1. Decrease in the area of the cathodic particles in the metal.	1. Increased stability of zinc, aluminum, magnesium, iron, and some other metals in solution of HCl, H_2SO_4 (for Mg and Al also in NaCl) with increased purity of the metal. Transfer of cathodic impurities into solid solution, for example during hardening of carbon steel or duralumin.
		2. Introduction of additives to the alloy, to increase the overpotential of the cathodic depolarization reaction.	2. Amalgamation of technical zinc with cadmium. Alloying technical magnesium with manganese. Alloying steel with As, Sb, Bi.
	Change in factors concerned with the surface of the article.	1. Metallic coverings with high values for the overpotential of the cathodic depolarization reaction.	1. Covering steel articles with cadmium or zinc (for use in acid solutions.
		2. Non-metallic coverings which either increase the overpotential of the cathodic depolarization reaction or hinder the diffusion of cathodic products into the layer.	2. Suggested mechanism for the effect of some oxide and hydroxide films on iron surfaces.
	Change in surrounding factors (surrounding conditions or corrosion medium).	1. Introduction of cathodic inhibitors into the solution.	1. As, Bi, Sb when etching iron in acids.
		2. Reduction of the concentration of cathodic depolarizers at the cathode.	2. Increased pH of the medium. Decreased O_2 in the solution. Decreased rate of stirring of the solution.
		3. Cathodic electrochemical protection(deceleration of cathodic processes consequent upon absorption of cathodic depolarizers by an external polarization current).	3. Cathodic polarization with an external current, use of protectors (protection of iron and steel constructions in neutral, aerated, corrosion media).
Increase in anodic control	Change in internal factors (metal)	1. Alloying to increase the anodic passivity of the alloy.	1. Alloying of iron or nickel with chromium. Alloying stainless steel with Ti, Nb, Ta.
		2. Introduction of active cathodes into the alloy (in conditions in which passivation is possible).	2. Alloying stainless steel with small amounts of Cu, Ag, Pd, or Pt. Introduction of Cu into low alloy steel (increased passivity of copper steel under atmospheric conditions).

TABLE (continued)

Change in the accelerating or retarding factors of the corrosion process	General character of the preventive measures	Concrete examples of anticorrosive protections	Practical examples of the protective method
1	2	3	4
	Change in factors concerned with the surface of the article.	1. Treatment of the metal surface to render it more passive.	1. Polishing the surface of stainless steel.
		2. Covering the article with a compact layer of a metal with greater ability to become passive.	2. Covering iron with chromium.
		3. Use of a paint layer or an oil containing a passivating pigment	3. Introduction of zinc-chromium pigments into paints or oils (protection from atmospheric corrosion).
	Change in surrounding factors (surrounding conditions or corrosion medium).	1. Introduction of anodic inhibitors or, in general, creation of a surrounding medium more capable of rendering the metal passive.	1. Introduction of pacifying anions (chromates, nitrates, vitrites, etc.,).
		2. Anodic electrochemical protection (deceleration of the anodic processes consequent upon passivity).	2. Anodic polarization by an external current. Contact with a more positive metal (for example a non compact cathodic covering).
Increase in ohmic control.	1. Change in internal factors (metal).	1. It is obviously impossible to cite an example of increased corrosion stability due to spontaneously increased ohmic resistance of the metal itself, except in some systems which include metallic semiconductors.	
	2. Change in factors concerned with the surface of the article.	2. It is possible that some isolated protective coverings increase the corrosion stability by ohmic deceleration.	
	3. Change in surrounding factors (surrounding conditions or corrosion medium).	3. Change in the surrounding medium to make possible increased ohmic resistance.	1. Drainage of soil to reduce subterranean corrosion under the influence of a macroscopic cell. Elimination of moisture from liquid oils to lower their corrosive activity.

SUMMARY

1. A more scientifically rational classification of the different methods of protection (against corrosion) is introduced, starting from their influence on: decreasing the degree of thermodynamic instability of the system, deceleration of the cathodic process, deceleration of the anodic process, or increasing the ohmic resistance of the system.

2. In the general case the effective methods of protection are those which affect the process which controls the basic corrosion process.

3. Simultaneous use of several protective methods with the same basic controlling factors increases their general effectiveness, but with different controlling factors the overall effectiveness may sometimes decrease.

4. Possible protective methods, which decrease the degree of thermodynamic instability, will always be able to decrease corrosion, but the effect of these methods will be less effective if the overall total retardation in the system is very large.

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EFFECT OF HYDROXIDE PRECIPITATION CONDITIONS ON THE MECHANICAL STRENGTH OF ALUMINA

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The development of processes employing fluidized catalyst beds, which are finding increasingly wide application in the petroleum processing and chemical industries, necessitates the production of catalysts with the mechanical strength needed for such processes. For the development of a method of producing mechanically strong aluminum–nickel and aluminum–molybdenum hydrogenation catalysts for the destructive hydrogenation of petroleums and petroleum residues under moderate pressure, investigations were carried out in the Institute of Petrochemical Synthesis of the Academy of Sciences of the USSR to determine the relation between the strength of these catalysts and the preparation conditions.

Catalysts based on alumina may be regarded as mixtures of the active component and alumina with a predominant content of the latter (85-99%). Therefore, the structure and mechanical strength of the alumina will determine the relevant properties of the alumina–oxide catalysts to a considerable extent. The structure of alumina changes considerably in relation to the preparation conditions and, in particular, the precipitation conditions: medium pH, temperature, rate of mixing of reagents, etc. [1-4].

The literature contains only isolated reports on the preparation of alumina and catalysts that are strong when operating in a stationary bed.* There has been no systematic investigation of the effect of various factors on the strength of alumina.

The development of a method of producing mechanically strong alumina and catalysts based on it, was based on the idea that one of the decisive factors in the strength is homogeneity of structure. An analysis of literature data from this point of view indicates that strong alumina should be obtained under conditions guaranteeing sufficiently complete decomposition of the basic salts which are formed during the precipitation of the hydroxide. On the other hand, the formation of a weakly hydrated, coarsely crystalline precipitate is apparently undesirable as thermal treatment of this yields alumina with a large number of macropores (low bulk density), which must reduce the strength. To check these hypotheses, we investigated the effect of medium pH, temperature, and rate of mixing of reagents during the precipitation of aluminum hydroxide.

EXPERIMENTAL

The aluminum hydroxide was precipitated by adding a 2 N solution of sodium hydroxide to a 2 N solution of chemically pure aluminum sulfate with stirring. The solution temperature was varied from 20 to 90°. When the required pH was reached (the pH was determined with a pH meter with a glass electrode), the precipitate was washed with cold distilled water, and adjusted with ammonia to the same pH as the mixture at the end of the precipitation. The precipitate was heated before washing in a number of experiments. The washing was carried out on a Buchner funnel with the continuous addition of water and stirring until the wash water contained traces of SO_4^{2-}. The washed and pressed out precipitate was formed manually into balls 5-6 mm in diameter, which were dried first in air (24 hr), then in a steam atmosphere at 60-70° (6 hr), and finally in a drying cupboard at 100-120° (6 hr). The dried balls were fired in a muffle furnace at 700° for 2 hr with the temperature raised to 700° over a period of 2-3 hr. The

* These problems were examined in the investigations of Yu. A. Bitepazh and G. K. Boreskov and their co-workers.

sulfate ion content, bulk weight, cracking strength [5], abrasion resistance [5], specific surface [1], and total porosity of the fired alumina were determined.

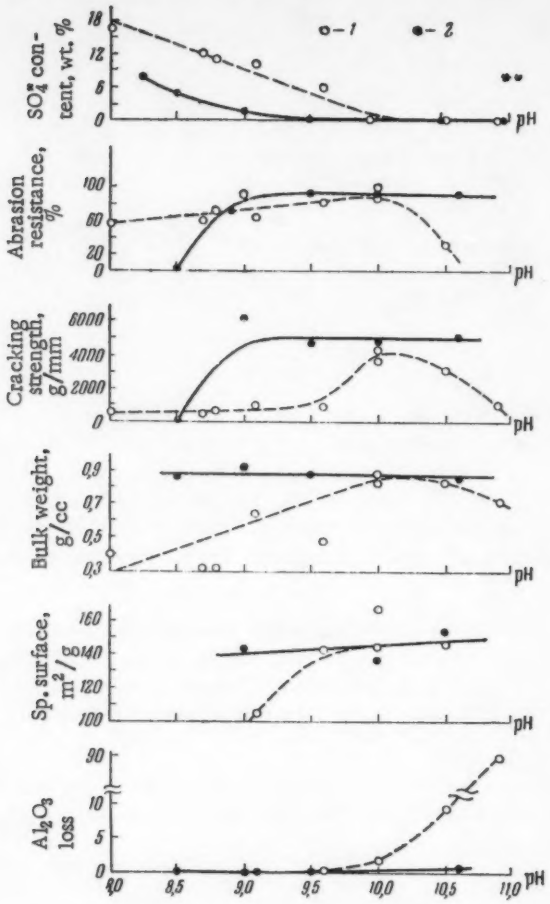

Fig. 1. Effect of medium pH during precipitation on the properties of alumina: 1) precipitation at room temperature (precipitation time 25-27 min); 2) precipitation at room temperature and heating at 70° with pH adjustment (precipitation time 30 min, heating time 100 min).

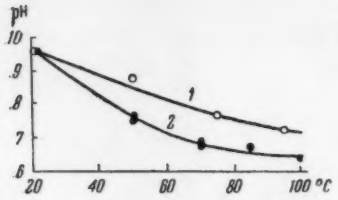

Fig. 2. Effect of precipitation and heating temperatures on the pH of the pulp (alkali consumption 96% of equivalent): 1) relation of pulp pH to temperature of solutions on precipitation; 2) relation of pulp pH to precipitate heating temperature.

The effect of medium pH on the properties of aluminum hydroxide and alumina was investigated over the pH range from 8 to 10.9 as precipitates obtained at pH values below 8 contained more basic aluminum sulfates than hydroxide [1]; in an alkaline medium (pH values above 10), there is appreciable solution of alumina with the formation of sodium aluminate [6]. An increase in the alkalinity of the medium increased the decomposition of the basic sulfates: the $SO_4^{"}$ content of the alumina decreased from 16% at pH 8 to 0 at pH 10 (Fig. 1). An increase in the degree of chemical homogeneity of the precipitate was accompanied by an increase in the bulk weight and mechanical strength of the alumina. The abrasion resistance increased from 57 to 98% and the cracking strength from 1000 to 4000 g/mm diameter of the ball. A further increase in the pH of the medium from 10 to 10.9 led to a fall in the bulk weight and strength. The latter may be connected with destruction of the structure of the hydrated precipitate due to the beginning of solution of aluminum hydroxide under these conditions: the loss of alumina with the mother solution was 0.1% at pH 9.1, 2% at pH 10, and ~90% at pH 10.9.

A rise in temperature, like an increase in the alkalinity of the medium, accelerated the hydrolysis of the basic salts. This appeared as a decrease in the pH of the pulp (Fig. 2) and a decrease in the $SO_4^{"}$ content of the alumina (Fig. 3) as a result of heating, regardless of whether the previously precipitated pulp was heated or whether the aluminum hydroxide was precipitated from hot solutions. However, the latter circumstance affected the strength of the alumina. The properties of samples obtained from hot solutions differed little from those of a sample precipitated at room temperature: they all had a low bulk weight of ~0.5 g/cc, cracking strength of ~1000-1200 g/mm, and abrasion resistance of 80-90%. The low cracking strength of these samples at a low basic sulfate content (3.2-3.8%) is connected with the precipitation from hot solutions of macrocrystalline aluminum hydroxide, which gives a weak oxide after thermal treatment.

Heating a pulp precipitated in the cold led to more substantial changes in the properties of the alumina. With an increase in the heating temperature, there was an increase in the bulk weight and cracking strength, though with

some samples of this series, the balls disintegrated during thermal treatment. Heating a pulp with pH adjustment during heating* with the pH kept at 9.5 by the addition of alkali as it reacted with the basic sulfates, made it possible to obtain the most pure alumina (sulfate ion content ~0.4%) with a high mechanical strength and none of the balls disintegrated during thermal treatment. The greatest changes in the properties of the samples occurred with heating to 50°. A further increase in temperature did not have an appreciable effect.

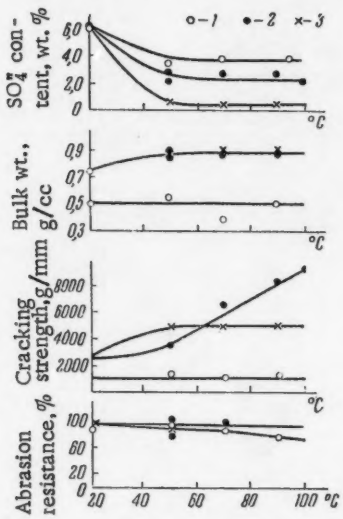

Fig. 3. Effect of temperature during hydroxide preparation on the properties of alumina: 1) precipitation from hot solutions; 2) heating of pulp precipitated in the cold (without adjustment of pH); 3) heating of pulp precipitated in the cold (with adjustment of pH).

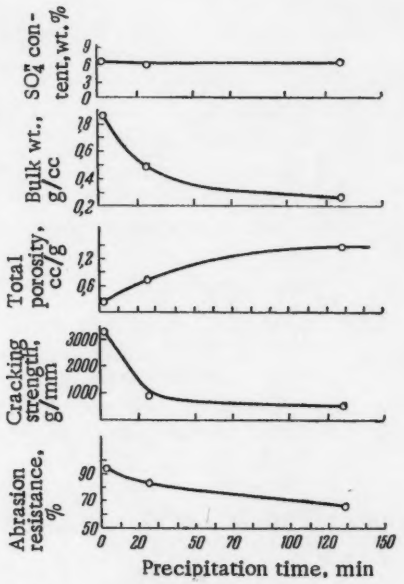

Fig. 4. Effect of hydroxide precipitation time on the properties of alumina.

The series of experiments with different values of the medium pH during precipitation was repeated under the optimal temperature conditions, namely, precipitation at room temperature and heating at 70° with adjustment of the pH of the pulp to the given value. The use of this precipitation procedure extended the pH range (9.0-10.5) over which it was possible to precipitate mechanically strong and quite pure alumina as there was quite complete decomposition of the basic sulfates even at pH 9.0 as a result of heating. Heating also promoted hydrolysis of the aluminate so that there was a sharp fall in the loss of alumina with the mother solution at pH values above 10 (Fig. 1).

The effect of the rate at which the reagents were mixed was investigated for samples precipitated at room temperature and pH 9.5. With an increase in the rate of mixing of the reagents or, what is the same thing, a decrease in the precipitation time, there was an increase in the bulk weight and mechanical strength of the alumina with the same content of basic sulfates (7% of $SO_4^{=}$) in all the samples (Fig. 4).

To study the relation between the structure and activity of the catalysts, it seemed interesting to prepare samples of alumina of low bulk weight, but free from basic sulfates. For this purpose we carried out experiments in which the temperature conditions, rate of mixing of the reagents, and pH of the wash water were varied (Table 1). By precipitation of aluminum hydroxide at room temperature and pH 9.5 over a period of 155 min and heating it to 70° it was possible to reduce the sulfate ion content to traces, but there was then a sharp increase in the bulk weight to 0.82 g/ml. When a pulp, precipitated under the conditions of experiment 402, was washed with ammonia solution of pH 10, the $SO_4^{=}$ content was reduced to 1.27%, while the alumina had a bulk weight of 0.32 g/cc. Samples with a low bulk weight (0.41 and 0.27 g/cc) and traces of sulfate ions were obtained by slow precipitation of the hydroxide from a hot (70°) salt solution. Samples with a low bulk weight had a low mechanical strength.

Preparation of mechanically strong alumina at constant pH. Under industrial conditions, aluminum hydroxide is usually precipitated by the simultaneous addition of reagents and precipitant, i.e., at constant pH. In this

*As in previous series, the alkali consumption in precipitation was 96% of the equivalent amount.

connection, we used parallel mixing of the reagent solutions on a laboratory apparatus to prepare alumina under the conditions that were optimal for precipitation at a varying pH, namely, precipitation at room temperature and heating at 70° for 1.5-2.0 hr with a pH of 9.5 for precipitation and heating. The alumina precipitated at constant pH did not contain SO_4^{2-} (Table 2). The mechanical strength, bulk weight, and specific surface were independent of the method of mixing the reagents.

TABLE 1. Preparation of Alumina Samples with Various Bulk Weights

Experiment No.	402	410	406	408	409
Preparation conditions					
Precipitation: salt solution temperature, °C	20	20	20	70	70
Alkali solution temperature, °C	20	20	20	20	20
Pulp temperature, °C	20	20	20	70	70
Time, min	129	135	155	135	176
Pulp pH at end	9.5	9.5	9.5	9.7	9.5
Heating: temperature, °C	20	20	70	70	70
Time, min	6	23	25	5	5
Pulp pH at end	9.5	9.5	9.5	9.7	9.5
Wash water pH	9.5	10	9.5	9.5	9.5
Characteristics of alumina					
Sulfate ion content, wt. %	7.0	1.27	Traces	Traces	0.38
Bulk weight, g/cc	0.27	0.32	0.82	0.41	0.27
Abrasion resistance, %	67	–	94	91	–
Cracking strength, g/mm ball diameter	500	700	6900	1000	1100
Specific surface, m/g	134	–	154	136	280
Total porosity, cc/g	1.49	1.26	0.32	0.92	1.55

TABLE 2

Experiment No.	394	404	405
Precipitation method	at varying pH	at constant pH	
Characteristics of alumina			
SO_4^{2-} content, wt. %	0.25	0.00	0.00
Bulk weight, g/cc	0.89	0.86	0.88
Abrasion resistance, %	93	98	98
Cracking strength, g/mm ball diameter	4700	4900	5300
Specific surface, m^2/g	–	150	155
Total porosity, cc/g	0.24	0.27	0.28

SUMMARY

1. One of the conditions for the formation of mechanically strong alumina is chemical homogeneity of the hydroxide precipitate. The degree of chemical homogeneity (completeness of decomposition of basic aluminum salts) is determined by the pH of the medium and the temperature during precipitation.

2. With the same degree of chemical homogeneity of the alumina, the strength of the latter falls with an increase in porosity.

3. Optimal conditions are given for the preparation of mechanically strong alumina.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

STERIC HINDRANCE AND CONFORMATION OF MOLECULES

COMMUNICATION 4. CRYSTAL STRUCTURE OF TETRABROMO-m-XYLENE AND TETRABROMO-o-XYLENE

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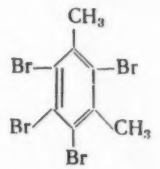
For studying the effect of steric hindrance on the conformation of molecules, it is interesting to investigate the structures of hexa-substituted benzenes with large substituents. In actual fact, in this case, the strain may be relieved in only one way, which is simple to describe, namely, the substituents are forced out of the plane of the nucleus alternately up and down, possibly with deformation of the nucleus itself. Literature data on the conformations of such molecules are contradictory and therefore we considered it expedient to carry out a structural investigation of several characteristic hexa-substituted benzenes taking tetrabromo-m-xylene as the first example.

EXPERIMENTAL

The crystals of tetrabromo-m-xylene (2,4,5,6-tetrabromo-1,3-dimethylbenzene)



we used for the investigation were very fine yellowish needles. The long direction of the needle was the b axis, the simple forms were pinacoids {100}, {101}, and {001}; the head faces were not developed. The monoclinic angle according to goniometric measurements was $\beta = 117°08' \pm 0°08'$. Determination of the parameters of the elementary cell from oscillation x-ray diffraction patterns led to the following values:

$a = 8,25 \pm 0,05$ Å $M = 421,8$
$b = 3,96 \pm 0,02$ Å $N = 2$
$c = 17,24 \pm 0,07$ Å $d_{x\text{-ray}} = 2,79$ g/cc
$V = 502$ Å^3

Systematic extinctions determined the space group unequivocally as $C_{2h}^5 = P2_1/c$, the two-fold positions of which have the symmetry 1. Consequently, the molecules lie at a center of inversion. Since the natural symmetry of the molecule (mm) does not contain a center, this indicates that the structure is characterized by statistical disorder of the positions of the substituents: we are not dealing with two chemically different types of substituents, Br and CH_3, but three crystallographically different "mean" substituents X_1, X_2, and X_3, where X = 2/3 Br + 1/3 CH_3. The two "effective" substituents 4/6 Br and 2/6 CH_3, which lie at each carbon atom of the nucleus, merge due to the similarity of the C–Br and C–C distances, i.e., are not resolved by an electron density series. Therefore, each carbon atom bears only one "mean" substituent X. This will be examined in more detail in the description of the structure.

To determine the coordinates of the atoms, we used a reciprocal lattice camera (unfiltered copper radiation) to obtain h0l and h1l scans with 81 and 181 reflections of measureable intensity, respectively. The intensities of the reflections were estimated visually from the blackening with an accuracy of ~10%. Only the polarization and Lorentz factors were considered in converting the intensities into structure factors.

The determination of the structure was begun with calculation of the projection of the interatomic function on the ac face; the coordinates of the substituents X_1, X_2, and X_3 found from it were used for determining the signs of the structure amplitudes. We then calculated the electron density projection $\rho(x,z)$, which showed all the carbon atoms of the benzene ring in addition to the substituents. We recalculated the structure amplitudes with allowance for all the atoms already resolved and using the atomic curves of Viervoll and Ögrim [1]. The atomic number of the mean substituent was taken as equal to

$$26 = \frac{2}{3} Z_{Br} + \frac{1}{3} Z_{CH_3}$$

The atomic curve of Fe was therefore used for the substituent. With the signs of these calculated structure amplitudes, we recalculated the approximation $\rho(x,z)$, shown in Fig. 1. The new coordinates of the atoms were determined by exponential interpolation [2]. The structure amplitudes calculated from these coordinates had the same signs as the previous series F_{calc} so that calculation of a third approximation $\rho(x,z)$ was pointless. The value of F_{calc} (second series) was used to calculate the theoretical electron density projection, which was used to introduce corrections for termination (by Booth's method) into the coordinates found from the second electron density projection. The "true" coordinates were found in this way (Table 1). A comparison of F_{meas} and F_{true}, which was calculated from the "true" coordinates, led to the following discrepancy factor and temperature correction: R = = 18.6%: B = 0.40 A^2.

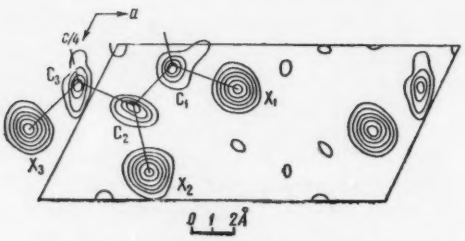


Fig. 1. Electron density projection. Contours are given for 2, 4, 6, and 8 el/A^3 for the C atoms and at 2, 10, 20, 30, 40, and 50 el/A^3 for the substituents.

The "true" coordinates were used to calculate the y coordinates, assuming a planar centrosymmetrical model with identical lengths for all the chemically equivalent bonds and valence angles of 120°:

$$y_C = \sqrt{D_{C-C}^2 - \Delta_{xz}^2}$$

$$y_x = \sqrt{(D_{C-C} + D_{C-X})^2 - \Delta_{xz}^2}$$

where D_{C-C} = 1.40 A and Δ_{XZ} is the projection of the corresponding distance on ac. The value of D_{C-X} was found from the formula (the C–Br and nucleus carbon-methyl group bond lengths were taken to be as follows: D_{C-Br} = 1.85 A and $D_{C-C'}$ = 1.52 A)

$$D_{C-X} = \frac{2 \cdot D_{C-Br} + 1 \cdot D_{C-C'}}{3} = \frac{2 \cdot 1{,}85 + 1{,}52}{3} = 1{,}74 \text{ Å},$$

while the accurate value was taken as the mean, weighted to allow for the atomic numbers

$$D_{C-X} = \frac{2 \cdot Z_{Br} \cdot D_{C-Br} + 1 \cdot Z_{CH_3} \cdot D_{C-C'}}{2 \cdot Z_{Br} + 1 \cdot Z_{CH_3}} = 1{,}82 \text{ Å}.$$

The values of y found in this way are given in Table 1. We designate these values, which were calculated for a planar model from data of the ac projection, by y_0.

We then refined y_0 by the method of least squares from reflections of the hl$l$ type. The structure amplitudes F_{hll} were calculated with the same assumptions as for F_{h0l}. With calculation of F_{calc} from y_0 only with allowance for the substituents X, the discrepancy factor R = 51.3%.

In accordance with the generally accepted way of using the method of least squares [3], the "best" values of the atomic parameters are those which give the minimum value of

$$\Sigma w(hkl) [|F_{meas}(hkl)| - |F_{calc}(hkl)|]^2$$

where w(hk$l$) is the "weight" of each term, which is normally taken as inversely proportional to the square of the

probable error in the corresponding F_{meas}. The condition for the minimum in the general form is as follows:

$$\sum w(F_{meas} - F_{calc})\frac{\partial F_{calc}}{\partial y_n} = \sum w\left\{\frac{\partial F_{calc}}{\partial y_n}\frac{\partial F_{calc}}{\partial x_n}\Delta x_n + \left(\frac{\partial F_{calc}}{\partial y_n}\right)^2 \Delta y_n + \right.$$
$$\left. + \frac{\partial F_{calc}}{\partial y_n}\frac{\partial F_{calc}}{\partial z_n}\Delta z_n + \frac{\partial F_{calc}}{\partial y_n}\left[\frac{\partial F_{calc}}{\partial x_m}\Delta x_m + \frac{\partial F_{calc}}{\partial y_m}\Delta y_m + \frac{\partial F_{calc}}{\partial z_m}\Delta z_m\right]\right\} \quad (1)$$

However, if the atoms are well resolved, it can be shown that such values as

$$\sum w\frac{\partial F_{calc}}{\partial y_n}\frac{\partial F_{calc}}{\partial x_m}$$

in most cases should be very small in comparison with the value $\Sigma w(\partial F_{calc}/\partial y_n)^2$. If the axes are orthogonal or almost orthogonal, then the values $(\partial F_{calc}/\partial y_n)(\partial F_{calc}/\partial x_n)$ etc., may be neglected also. Equation (1) then assumes the form

$$\Delta y_n \sum w\left(\frac{\partial F_{calc}}{\partial y_n}\right)^2 = \sum w(F_{meas} - F_{calc})\frac{\partial F_{calc}}{\partial y} \quad (2)$$

In our case, the condition of orthogonality is fulfilled (the y axis is perpendicular to the plane of the other two axes). We adopted only two values for the weight function (w = 0 for reflections with $F_{meas} = 0$ and for reflections with strongly diverging F_{meas} and F_{calc}; for the other reflections, w = 1) and used the simplified condition for the minimum (2) for the calculation. For our case of symmetry

$$F(h\,1\,l)\begin{cases}\Sigma f_i \cos 2\pi(hx_i + lz_i)\cos 2\pi y_i & \text{where } l = 2n+1\\ -\Sigma f_i \sin 2\pi(hx_i + lz_i)\sin 2\pi y_i & \text{where } l = 2n\end{cases}$$
$$\partial F/\partial y_i = -2\pi \cos 2\pi(hx_i + lz_i)\sin 2\pi y_i \text{ where } l = 2n+1$$
$$\partial F/\partial y_i = -2\pi \sin 2\pi(hx_i + lz_i)\cos 2\pi y_i \text{ where } l = 2n$$

In the first stage, we refined only the values y_X. In the second stage of the refinement, all the atoms were considered, X with the coordinates y_1 and the carbon with the coordinates y_0. A comparison of F_{meas} with F_{calc}, calculated from the refined y_2 coordinates, gave R = 32.0% and B = 1.48 A^2. The changes in the coordinates y during the refinement are shown in Table 2.

TABLE 1. Atomic Coordinates from ac Projection

Atom	x_{true}	y_0	z_{true}
X_1	0,414	0,152	0,144
X_2	0,278	0,000	0,414
X_3	—0,135	—0,214	0,272
C_1	0,183	0,083	0,068
C_2	0,124	0,000	0,188
C_3	—0,070	—0,057	0,118

TABLE 2. Refinement of Coordinates y

Atom	y_0	y_1	y_2
X_1	0,152	0,216	0,232
X_2	0,000	—0,051	—0,057
X_3	—0,214	—0,270	—0,275
C_1	0,083		0,086
C_2	0		—0,078
C_3	0,057		—0,038

The values of x_{true}, z_{true}, and y_2 corresponded well with the planar model of the molecule. In actual fact, on the basis of the coordinates obtained, we calculated distances (Ce is the center of the molecule): Ce—X = 3,227 ± ± 0,017 A; Ce—C = 1,432±0,048 A; X—X = 3,228±0,027 A. The equality of the distances Ce—X and X—X with the condition of centrosymmetry shows that the molecule is planar and has its own hexagonal symmetry. We were also convinced of the accuracy of the planar model by the fact that by taking the incorrect length of the C—X bond of 1,74 A initially for the calculation of y_0, we obtained as a result of refinement of y the true value of 1,82 A (formula given above. The final values of the coordinates obtained from the experiment are given in Table 3.

We then found the "ideal" coordinates of the substituent for the planar model. For this purpose, a right hexagon with the center at the center of symmetry, the substituents X at the apexes, and the X–X distances equal to the Ce–X distance = 3.227 A was rotated about the three orthogonal axes until the best agreement with the experimental positions of the substituents X was reached. The optimal orientation of the "ideal" model was found by the method of least squares. The values of the "ideal" coordinates found are given in Table 4.

TABLE 3. Experimental Values of Coordinates

Atom	x	y	z
X_1	0,414	0,232	0,144
X_2	0,278	—0,057	0,414
X_3	—0,135	—0,275	0,272
C_1	0,183	0,086	0,068
C_2	0,124	—0,078	0,188
C_3	—0,070	—0,038	0,118

It could be assumed that the discrepancy factor would be improved considerably by "resolving" the mean substituent X into Br and the CH_3 group. The coordinates of the Br atoms and CH_3 groups were found from the coordinates of the substituent by simple proportion.

$$x(y, z)_{CH_3} = \frac{D_{Ce-CH_3}}{D_{Ce-X}} \cdot x(y, z)_X$$

$$x(y, z)_{Br} = \frac{D_{Ce-Br}}{D_{Ce-X}} \cdot x(y, z)_X$$

$$x(y, z)_C = \frac{D_{Ce-C}}{D_{Ce-X}} \cdot x(y, z)_X$$

These coordinates are also given in Table 4 and were used to calculate all the interatomic distances given in the description of the structure. From them we calculated the structure amplitudes for reflections of the type $h0l$ and hll, using the individual atomic factors for Br and the CH_3 group (the atomic curve of nitrogen was used for it). In actual fact, the discrepancy factors were decreased considerably: $R_{h0l} = 12.7\%$; $R_{hll} = 18.4\%$.

TABLE 4. Final Values of Coordinates

Atoms	x, Å	y, Å	z, Å	Atoms	x, Å	y, Å	z, Å
X_1	3,452	0,915	1,214	$(CH_3)_1$	3,121	0,827	1,097
X_2	2,290	—0,204	3,532	$(CH_3)_2$	2,070	—0,184	3,193
X_3	—1,100	—1,119	2,320	$(CH_3)_3$	—1,049	—1,012	2,097
Br_1	3,473	0,921	1,222	C_1	1,496	0,397	0,526
Br_2	2,304	—0,205	3,554	C_2	0,993	—0,088	1,531
Br_3	—1,167	—1,126	2,334	C_3	—0,503	—0,485	1,006

As a measure of the accuracy of the determination of the interatomic distances we may take the spread we obtained in the crystallographically different, but chemically identical distances. Thus, for the X–X distance we obtain the error ± 0.02 A and for the C–C distance ± 0.05 A. This is more advantageous in the given case than the use of Vainshtein's formula, for example, as in using the latter it is difficult to allow for the effect of termination. The quite large error is apparently connected with the considerable break at termination and the effect of the absorption factor, which is unavoidable as compounds containing bromine are difficult to photograph with molybdenum radiation. As the molecule occupies a particular position, the accuracy of the determination of the distances for the "ideal" model should be considerably better: of the order of ± 0.01 A for the Br–Br distance and ± 0.02 A for the C–C distance.

Description of Structure

Two projections of the structure found are given in Figs. 2 and 3. The molecule of 2,4,5,6-tetrabromo-1,3-dimethylbenzene is planar with an accuracy of about ± 0.02 A. The equation of the beat plane passing through the substituents X_1, X_2, and X_3 is

$$-0.2442x + 0.9294y + 0.2762z = 0.$$

The angle of this plane to the ac plane $\delta = 21°39'$. The distances of the substituents from the plane are as follows: X_1 + 0.018 A; X_2 – 0.018 A; X_3 + 0.019 A. The line of intersection of this plane with the ac plane forms an angle of $\gamma = 48°31'$ with the 0z axis in the negative quadrant.

Within the limits of error, the length of the C–C bond agrees with the value 1.40 A given in tables. The C–Br and C–CH_3 bonds also apparently have the usual lengths of 1.85 and 1.52 A. Although we were unable to determine the lengths of these bonds experimentally because of the merging of the maxima of the CH_3 group and Br atom on the electron density projection, the weighted mean of these distances (1.82 A) agrees with the experimental value.

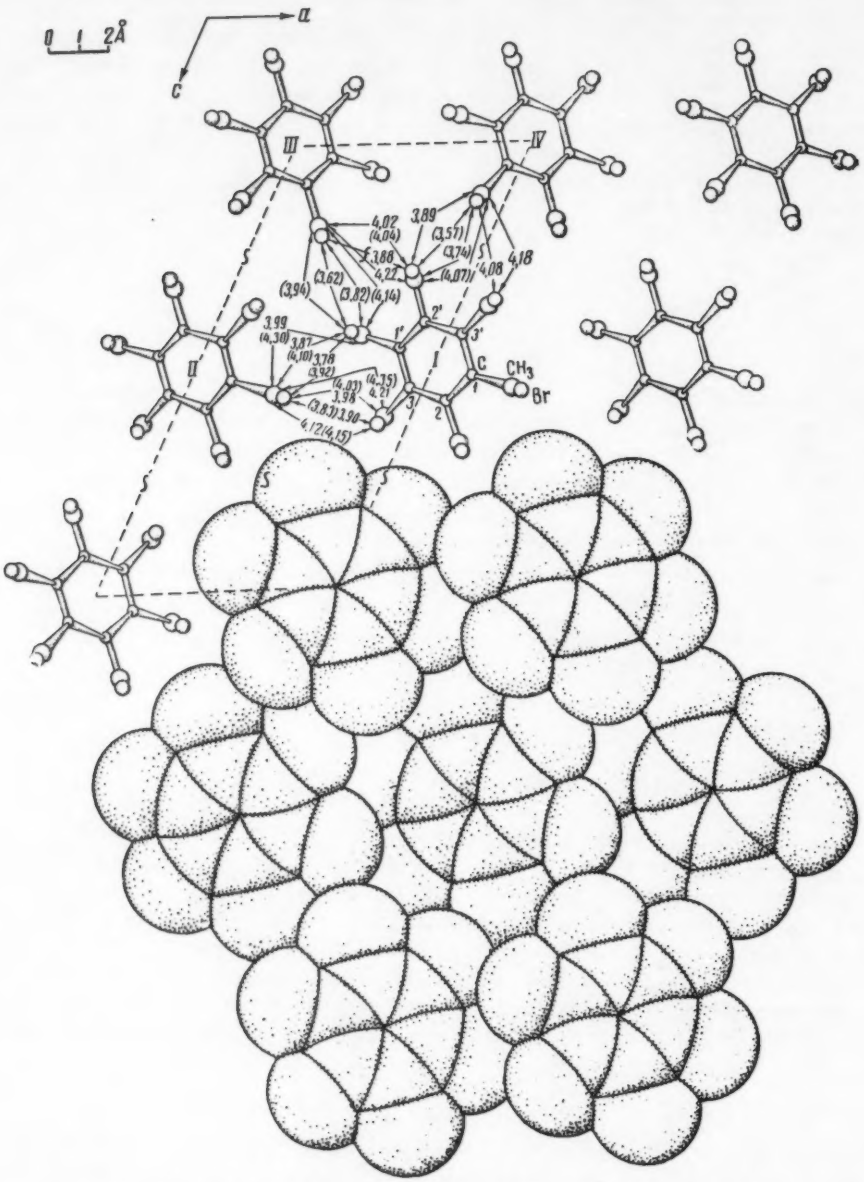


Fig. 2. Projection on ac of the structure of tetrabromo-m-xylene.

The planar molecule of tetrabromo-m-xylene with the ideal valence angles of 120° has substantial steric hindrance: thus, the Br–Br distance is 3.25 A, while twice the intermolecular radius of bromine equals 3.90 A (0.65 A contraction); the CH_3–Br distance is 3.10 A, while the sum of the intermolecular radii is 3.95 A* (0.75 A contraction). Data on other structures with sterically strained moles, though few (see, for example [4]), show that such

* As the intermolecular radius of the CH_3 group we took the mean of its dimensions in different directions (2.0 A).

steric hindrance may lead to distortion of the angles by 15-20°. In our case the steric hindrance would be decreased considerably by the substituents moving out of the plane of the benzene nucleus alternately up and down. Thereupon there could also be disruption of the coplanarity of the nucleus itself: it would acquire the configuration of a chair with the sysmetry $\bar{3}$m instead of 6/mmm. Theoretical calculation by the method proposed by Kitaigorodskii [5] requires the displacement of the Br atom and CH_3 group by 0.53 A and the carbon atom of the benzene nucleus by 0.06 A from the plane. The displacement from the plane would be alternately up and down so that the molecule would acquire a chair conformation.

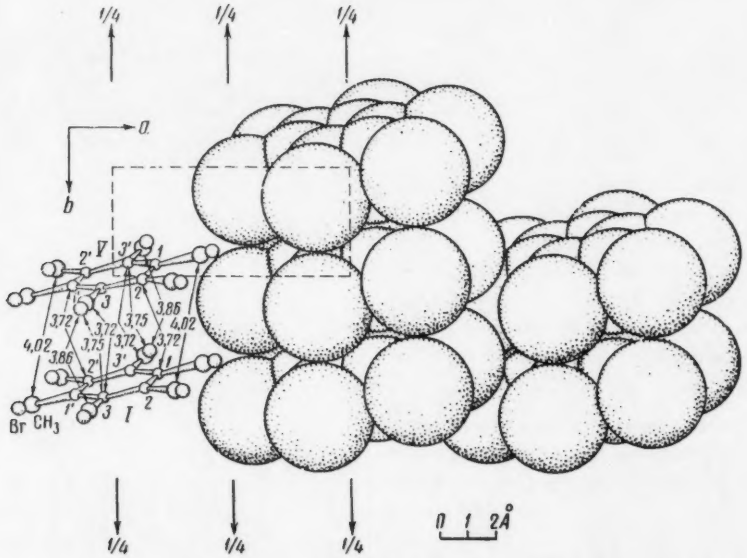


Fig. 3. Projection on ab of the structure of tetrabromo-m-xylene.

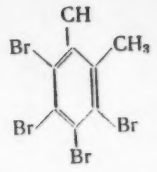
However, according to our investigation, the molecule is planar.* This may be explained by the specific effect of the force field on the crystal. Similarity of the deformation energy of the valence angles (steric hindrance) and the energy of the intermolecular interaction in the crystal obviously indicates the possibility of a difference in the conformations of the free molecule and the molecule in the crystal, which is actually observed with biphenyl, for example [4]. Therefore, theoretical calculations of the conformation of free molecules, generally speaking, are applicable to molecules in a crystal only with certain limitations. Conclusions on the conformations of free molecules should be drawn with great care from the results of a structural investigation of crystals. Moreover, in principle, a comparison of theoretical calculations with experimental results for crystals makes it possible to investigate the force field of the crystal by means of the distortions it introduces into the conformation of the molecule.

It may be that the simplified calculation method used at the present time is not applicable to hexa-substituted benzenes, the more so as other analogous molecules (hexachlorobenzene and hexamethylbenzene) are also planar according to literature data [5]. It is true that the conclusions on the structure of these molecules are based on inadequate experimental data (one electron density projection). We hope to refine the data on these structures by an objective determination of the y coordinates.

The structure of tetrabromo-m-xylene is characterized by statistical disorder in the sense that the substituents, the Br atom and the CH_3 group, statistically occupy the same positions in the cell. This is connected with the very

* Since the molecule of tetrabromo-m-xylene is inclined to the plane of the main projection ac by a small angle and the y coordinates were refined, starting from a planar model, there is the danger that the experiment would be unable to "resolve" two nonplanar centrosymmetrical molecules with a chair configuration alternating through the crystal and derived from each other by rotation about a third order axis by 120°. However, these two molecules practically merge on the ac projection. Therefore we attempted to "split" our planar molecule into two molecules with chair configurations. All the atoms were "split" into two, one moved up and the other down normal to the plane of the molecule by the theoretical distance (see above). "Refinement" of the y coordinates by the method of least squares for this model showed its inaccuracy as the discrepancy factor for reflections of the type hl$\bar{l}$ rose to 52.4%.

similar intermolecular radii of the Br atom (1.95 A) and the CH_3 group (2.00 A). It could be surmised that tetrabromo-o-xylene (3,4,5,6-tetrabromo-1,2-dimethylbenzene) would have the same structure as tetrabromo-m-xylene.



Investigation of tetrabromo-o-xylene crystals showed that within the limits of experimental error, the parameters of the elementary cell coincided completely with the data for tetrabromo-m-xylene. A comparison of structure amplitudes of reflections of the type h0l (Fig. 4) showed that they also coincided with the normal accuracy. The same disorder for the same reasons characterizes the structure of 1,2-dichlorotetramethylbenzene [6].

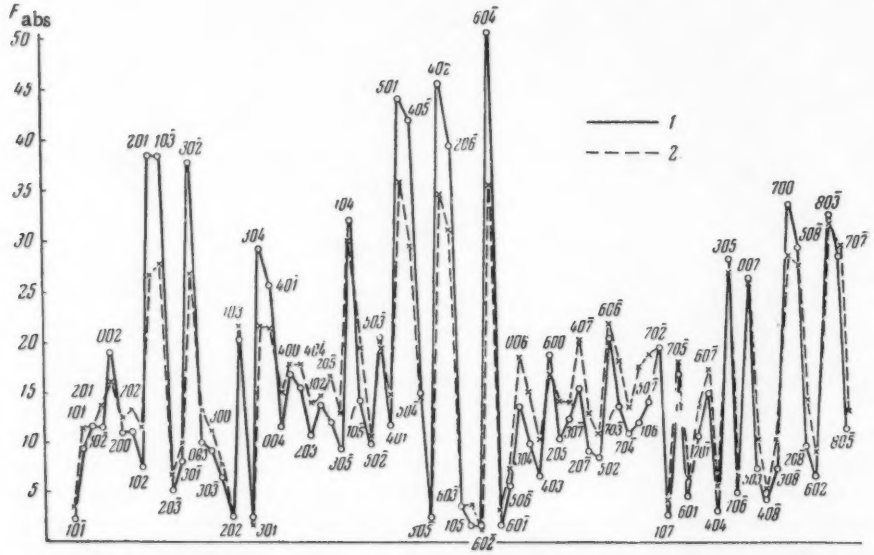


Fig. 4. Comparison of F_{meas} of ortho- (2) and meta- (1) tetrabromoxylenes.

The shortest intermolecular distances are given in Table 5. The molecules are numbered in accordance with Figs. 2 and 3.

I is the starting molecule with the center at (000).

II is a molecule derived with translation a with the center at ($\bar{1}$00).

III is a molecule derived with the axis 2_1 [−1/2, y, −1/4] with the center at (−1, 1/2, −1/2).

IV is a molecule derived with the axis 2_1 [0, y, −1/4] with the center at (0, 1/2, −1/2).

V is a molecule derived with translation b with the center at (010).

These distances lead to the following intermolecular radii:

$$R_C = 1.90 \pm 0.05 \text{ A}; \; R_{Br} = 1.95 \pm 0.01 \text{ A}; \; R_{CH_3} = 2.08 \pm 0.08 \text{ A}$$

The radius of the effective mean substituent $R_X = 1.99$ A. The values of R_{CH_3} and R_{Br} practically coincide with the generally accepted values; the radius of the carbon atom is high by 0.1 A (it is possible that the carbon atoms do not participate in intermolecular contacts). The disorder of the structure is explained by the similarity of the radii of the bromine and methyl group, as a result of which their interchange has hardly any effect on the number and nature of the intermolecular contacts, i.e., the internal energy, while the entropy term in the free energy increases substantially.

The molecules form densest layers of the type t_1t_2 [$\bar{1}$] with coordination 6, parallel to ac [4]. These layers are superposed also in the densest way through, for example, centers of symmetry of the form $\underline{1}$ (0, 1/2, 0), creating packing with the coordination number 14. The volume of the molecule, calculated from the intermolecular radii found, V_0 = 439 A^3; the packing factor k = 0.88. This value is higher than the normal values for organic crystals. The reason is obvious – the volume of the molecule is high as no allowance was made for comparison of the intermolecular spheres due to steric hindrance. The problem of the "radii" of atoms whose electron shells are deformed by steric hindrance requires further investigation and, first of all, analysis of the relation between the intermolecular distances and the orientation of the corresponding vectors relative to the axes of the molecule.

TABLE 5. Intermolecular Distances (A)*

Atoms	Distance, d	Sum of radii, ΣR	ΣR − d	Atoms	Distance d	Sum of radii, ΣR	ΣR − d
$Br_{(2')}I$ — $Br_{(3)}IV$	(3,57)	3,90	0,33	$CH_{3(1)}II$ — $Br_{(1')}I$	(4,10)	4,03	—0,07
$Br_{(1')}I$ — $Br_{(2)}III$	(3,62)	3,90	0,28	$CH_{3(1)}II$ — $Br_{(3)}I$	4,12	4,03	—0,09
$Br_{(1')}I$ — $Br_{(1)}II$	0,78	3,90	0,12	$CH_{3(1')}I$ — $Br_{(2')}V$	(4,14)	4,03	—0,11
$Br_{(3)}I$ — $Br_{(1)}II$	(3,83)	3,90	0,07	$CH_{3(1)}II$ — $Br_{(3)}I$	(4,15)	4,03	—0,12
$Br_{(2')}I$ -- $Br_{(2)}III$	3,88	3,90	0,02	$CH_{3(3)}IV$ — $Br_{(3')}I$	4,18	4,03	—0,15
$Br_{(3)}I$ — $Br_{(1)}II$	3,90	3,90	0,00	$CH_{3(2)}V$ — $Br_{(3)}I$	(4,22)	4,03	—0,19
$Br_{(1')}I$ — $Br_{(1)}II$	(3,92)	3,90	—0,02	$CH_{3(1')}I$ — $CH_{3(1)}II$	3,99	4,16	0,17
$Br_{(3')}I$ — $Br_{(3)}IV$	4,08	3,90	—0,18	$CH_{3(1')}I$ — $CH_{3(2')}V$	(4,02)	4,16	0,14
$CH_{3(2')}I$ — $Br_{(3)}IV$	(3,74)	4,03	0,29	$CH_{3(2')}I$ — $CH_{3(3)}IV$	(4,07)	4,16	0,09
$CH_{3(1')}I$ — $Br_{(2)}III$	(3,82)	4,03	0,21	$CH_{3(1')}I$ — $CH_{3(2)}III$	(4,14)	4,16	0,02
$CH_{3(3)}V$ — $Br_{(3)}I$	(3,86)	4,03	0,17	$CH_{3(3)}I$ — $CH_{3(2)}V$	(4,20)	4,16	0,04
$CH_{3(1)}II$ — $Br_{(1')}I$	3,87	4,03	0,16	$CH_{3(3)}I$ — $CH_{3(1)}II$	4,21	4,16	0,05
$CH_{3(1')}V$ — $Br_{(1')}I$	(3,88)	4,03	0,15	$CH_{3(2')}I$ — $CH_{3(2)}III$	4,22	4,16	0,06
$CH_{3(3)}IV$ — $Br_{(2')}I$	(3,89)	4,03	0,14	$CH_{3(1')}I$ — $CH_{3(1)}II$	(4,30)	4,16	0,14
$CH_{3(2)}III$ — $Br_{(1')}I$	(3,94)	4,03	0,09	$CH_{3(3)}I$ — $CH_{3(1)}II$	(4,35)	4,16	0,19
$CH_{3(2')}V$ — $Br_{(2')}I$	3,95	4,03	0,08	$Br_{(3)}I$ — $C_{(3)}V$	(3,75)	3,85	0,10
$CH_{3(3)}I$ — $Br_{(1)}II$	3,98	4,03	0,05	$Br_{(1')}I$ — $C_{(1')}V$	(3,87)	3,85	0,02
$CH_{3(2)}III$ — $Br_{(2')}I$	4,02	4,03	0,01	$Br_{(3)}I$ — $C_{(2)}V$	(3,93)	3,85	0,08
$CH_{3(3)}I$ — $Br_{(1)}II$	(4,03)	4,03	0,00	$Br_{(1')}I$ — $C_{(2')}V$	(3,96)	3,85	0,11
$CH_{3(2)}III$ — $Br_{(2')}I$	(4,04)	4,03	—0,01	$CH_{3(3)}I$ — $C_{(3)}V$	(3,72)	3,98	0,26
$CH_{3(2')}V$ — $Br_{(1')}I$	(4,06)	4,03	—0,03	$CH_{3(1')}I$ — $C_{(1')}V$	(3,82)	3,98	0,16
$CH_{3(3)}I$ — $C_{(2)}V$	(3,84)	3,98	0,14	$CH_{3(2')}V$ — $C_{(1')}I$	(4,18)	3,98	0,20
$CH_{3(1')}I$ — $C_{(2')}V$	(3,85)	3,98	0,13	$C_{(1')}I$ — $C_{(2')}V$	(3,72)	3,80	0,08
$CH_{3(2')}I$ — $C_{(2')}V$	4,15	3,98	0,17	$C_{(3)}I$ — $C_{(2)}V$	(3,81)	3,80	0,01
$CH_{3(3)}I$ — $C_{(1')}V$	(4,15)	3,98	0,17	$C_{(3)}I$ — $C_{(1)}V$	(3,82)	3,80	0,02

* The figures in brackets give the distances between atoms of molecules connected with the compulsory participation of translation.

In conclusion, the authors would like to thank Prof. A. I. Kitaigorodskii for providing the result of a theoretical calculation of the conformation of the tetrabromo-m-xylene molecule and also Z. G. Volkova, V. V. Shkiperova, and K. F. Lugova for carrying out most of the calculations.

SUMMARY

1. We determined the space group and elementary cell parameters of tetrabromo-m-xylene and tetrabromo-o-xylene and the crystal structure of tetrabromo-m-xylene.

2. The structures of tetrabromo-o- and tetrabromo-m-xylene are identical and are disordered due to the similarity of the radii of the substituents, which statistically occupy the same position in the cell.

3. The tetrabromo-m-xylene molecule is planar with an accuracy of about ± 0.02 A. The intermolecular radii were obtained from the shortest intermolecular distances.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SEVERAL REACTIONS OF METHYL-β,β-DICHLOROVINYL KETONE

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Original article submitted September 21, 1959

One of us, Kochetkov, and Rybinskii and co-workers have in recent years studied the conversion of β-chlorovinyl ketones, and starting from them have achieved the syntheses of various classes of organic compounds [1]. As regards β,β-dichlorovinyl ketones, information on their chemical properties is lacking to a much greater extent. This fragmentary data is limited to the following reactions: oxidation of methyl-β,β-dichlorovinyl ketone with potassium hypobromite to β,β-dichloroacrylic acid [2], ozonolysis and subsequent hydrolysis to phosgene [2], several condensation reactions [3], reactions at the carbonyl (formation of semicarbazones, phenyl- and 2,4-dinitrophenylhydrazones) [2-5], reactions with organomagnesium compounds [3, 4], and finally, reduction with zinc in ethyl alcohol to methyl-β,β-dichlorovinyl ketone [3] and reaction of β,β-dichlorovinyl ketone with sodium ethylate [5]. The latter reaction is described by Julia as being a convenient method of preparing β-keto esters.

In the present work a systematic study was made of nucleophilic substitution of vinyl halogens in methyl-β,β-dichlorovinyl ketone. Chosen as nucleophilic reagents were sodium alcoholates, amines, salts of carboxylic acids, salts of benzenesulfinic and thiacetic acids, and finally, sodium thiocyanate, bromide, and cyanide. Reaction of methyl-β,β-dichlorovinyl ketone with sodium alcoholates leads to formation of dialkyl acetals of acetylketene, and not that of esters of acetoacetic acid, as described by Julia

$$HC_3COCH{=}CCl_2+2C_6H_5ONa\rightarrow CH_3COCH{=}C(OC_2H_5)_2+2NaCl.$$

The method worked out by us for reacting methyl-β,β-dichlorovinyl ketone with sodium alcoholates differs from Julia's method only in the manner of treating the reaction mixture. Julia diluted the reaction mixture with water, then acidified it with dilute sulfuric acid and extracted the β-keto ester obtained with ether. As is known [6], under these conditions the originally formed acetal of acetylketene is converted into an acetoacetic ester

$$CH_3COCH{=}C(OC_2H_5)_2\xrightarrow{OH_3^+}CH_3COCH_2CO_2C_2H_5+C_2H_5OH.$$

Even on treating the diethyl acetal of acetylketene with dry hydrogen chloride in absolute ether, this being undertaken by us with the aim of preparing a monochloro- substituted product, only the acetoacetic ethyl ester is obtained.

$$CH_3COCH{=}C(OC_2H_5)_2\xrightarrow{HCl}\left[CH_3COCH_2C(Cl)(OC_2H_5)_2\right]\rightarrow CH_3COCH_2CO_2C_2H_5+C_2H_5Cl$$

As the reaction product the formation was observed of a white, crystalline compound which in all probability is the addition product of hydrogen chloride to the diethyl acetal at the double bond.

Julia proposed the following scheme for formation of β-keto esters:

$$CH_3COCH{=}CCl_2+C_2H_5ONa\rightarrow CH_3COCH_2C(Cl)(OC_2H_5)-C\xrightarrow{C_2H_5ONa}$$

$$\rightarrow CH_3COCH_2CO_2C_2H_5+C_2H_5OC_2H_5+NaCl$$
$$\rightarrow CH_3COCH_2CO_2C_2H_5+NaCl+C_2H_5Cl$$

In presence of an alkaline catalyst, addition of an alcohol molecule takes place at the double bond; then formation of a β-keto ester can be postulated either by splitting off an ether and sodium chloride or, more likely, in Julia's opinion, by splitting off ethyl chloride.

In the light of our data, this mechanism can be represented in the following manner:

$$CH_3COCH=CCl_2+RONa\rightarrow CH_3COCH=C(OR)Cl+NaCl \quad (1)$$

$$CH_3COCH=C(OR)Cl+RONa\rightarrow CH_3COCH=C(OR)_2+NaCl \quad (2)$$

$$CH_3COCH=C(OR)Cl\xrightarrow{OH_3^+}CH_3COCH_2CO_2R+HCl \quad (3)$$

$$CH_3COCH=C(OR)_2\xrightarrow{OH_3^+}CH_3COCH_2CO_2R+ROH \quad (4)$$

With a stronger alkaline reagent – sodium isopropylate – complete resinification of the reaction mixture takes place, and with tertiary sodium butylate the reaction proceeds explosively. Under ordinary conditions, methyl-β,β-dichlorovinyl ketone does not react with the sodium salts of acetic, propionic, benzoic, and o-nitrobenzoic acids, with silver acetate, potassium bromide, nor with potassium diphenylamine and phthalimide. Amines such as diethylamine, triethylamine, pyridine, and piperidine have a dehydrohalogenating effect on methyl-β,β-dichlorovinyl ketone, the reaction mixture being completely resinified. Reaction with potassium cyanide also leads to resinification of the ketone.

Reaction with potassium thiocyanate according to the usual scheme for gradual substitution of chlorine atoms

$$2CH_3COCH=CCl_2+3KCNS\rightarrow CH_3COCH=C(SCN)Cl+$$
$$+CH_3COCH=C(SCN)_2+KCl$$

It is interesting to note the reaction of methyl-β,β-dichlorovinyl ketone with sodium benzenesulfinate in methanol. Besides a small amount of 1-chloro-1-phenylsulfonylbutenone-3, diphenylsulfonylmethane is formed as the main reaction product

$$2CH_3COCH=CCl_2+3C_6H_5SO_2Na\xrightarrow{H_2O}CH_3COCH=C\begin{matrix}SO_2C_6H_5\\Cl\end{matrix}+$$
$$+CH_2(SO_2C_6H_5)_2+3NaCl+CH_3COCHO\ (?)$$

Formation of diphenylsulfonylmethane can be explained in the following manner: 1,1-diphenylsulfonylbutenone-3 formed as an intermediate product under the reaction conditions undergoes rapid hydrolysis at the double bond

$$CH_3COCH=C(SO_2C_6H_5)_2\xrightarrow[NaHCO_3]{H_2O}CH_2(SO_2C_6H_5)_2+CH_3COCHO\ (?)$$

A similar tendency toward hydrolytic decomposition under very mild conditions is also noted for β,β-disulfonyl derivatives of ketones [7].

Methyl-β,β-dichlorovinyl ketone also reacts peculiarly with sodium thioacetate. As the sole reaction product a compound is obtained with empirical formula C_4H_4OS, which by analogy with the dimer of acetylketene – dehydroacetic acid, possibly has the structure of the dimer of acetylthioketene. Formation of such a product can be postulated in the following manner:

$$CH_3COCH=CCl_2\rightarrow\left[CH_3COCH=C\begin{matrix}Cl\\SCOCH_3\end{matrix}\right]\xrightarrow{H_2O}$$

$$\left[CH_3COCH=C\begin{matrix}Cl\\SH\end{matrix}\right]\xrightarrow{-HCl}(CH_3COCH=C=S)_2$$

EXPERIMENTAL

Methyl-β,β-dichlorovinyl ketone. Methyl-β,β-dichlorovinyl ketone was prepared according to the method described by Heilbron and Julia [4]. To 250 g (3.2 M) of acetyl chloride, cooled with ice, was added, by degrees, with vigorous stirring 424 g (3.2 M) of yellow anhydrous aluminum chloride. To obtain methyl-β,β-dichlorovinyl ketone it was necessary to use yellow aluminum chloride containing a trace of ferric chloride. With pure white aluminum chloride containing no impurities, yield of ketone fell abruptly to 5-10% theoretical. The mixture was placed in an ice bath and to it added dropwise over a period of 2.5 hr 309 g (2.2 M) of freshly distilled vinylidene chloride. On adding the first few drops of vinylidene chloride, the mixture assumed a dark-red color and soon became homogeneous and quite liquid, but toward the end of the addition became viscous again. After stirring for a further 2 hr, the reaction mixture was gradually poured into crushed ice (1.5 kg) with continuous stirring. Then the whole mixture was placed in a flask and steam-distilled. The lower organic layer was separated, dried over fused sodium sulfate at 0° in presence of a trace of hydroquinone and distilled in vacuo. The product had b. p. 56-58° (15 mm); $n^{19}D$ 1.4948. In the data in the literature [4]: b. p. 58° (15 mm); $n^{20}D$ 1.4940. In all, 345 g of methyl-β,β-dichlorovinyl ketone was obtained (78% theoretical, calculated on vinylidene chloride). Methyl-β,β-dichlorovinyl ketone was stored for a considerable time at 0° in presence of hydroquinone without decomposition.

Reaction of methyl-β,β-dichlorovinyl ketone with sodium ethylate. To 80 ml of absolute ethanol was gradually added 2.3 g (0.1 M) of metallic sodium. To the alcoholic sodium ethylate solution was added dropwise with constant stirring 13.8 g (0.1 M) of methyl-β,β-dichlorovinyl ketone. A crystalline precipitate of sodium chloride settled out; the reaction mixture took on a red color. After 15 minutes the reaction mixture was filtered from the mineral precipitate. A stream of carbon dioxide was passed through the alcoholic solution for 2 hr. The neutralized alcoholic filtrate was distilled in a flask fitted with a large dephlegmator. Alcohol was first distilled off, and the remainder distilled in vacuo. The following fractions were collected: I with b. p. 56-57° (27 mm); 10 g; II with b. p. 128-130° (18 mm); 8 g.

Fraction I was an azeotropic mixture of ethanol and initial methyl-β,β-dichlorovinyl ketone. The 2,4-dinitrophenylhydrazone of methyl-β,β-dichlorovinyl ketone was prepared from the mixture. Melting point after recrystallizing from benzene was 192-193°. Data in the literature [4]: m. p. 195°. No melting point depression was observed when a sample was mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of methyl-β,β-dichlorovinyl ketone. Fraction II was the diethyl acetal of acetylketene. After redistillation, b. p. was 135-136.5° (20 mm); $n^{19}D$ 1.4738; d^{19}_4 1.002. Data in the literature [8]: b. p. 138.5-140.5° (21 mm); $n^{25}D$ 1.4720; d^{25}_4 1.000. Found: C 60.61, 60.68; H 8.95, 8.87%. $C_8H_{14}O_3$. Calculated: C 60.77; H 8.85%.

Reaction of the diethyl acetal of acetylketene with dry hydrogen chloride in absolute ether. A stream of dry hydrogen chloride was passed 3 hr through a solution of 20 g of the diethyl acetal of acetylketene in 150 ml of absolute ether. A white, voluminous precipitate settled out, which on further passage of hydrogen chloride dissolved completely. Ether was evaporated off, and the residue distilled in vacuo. The sole reaction product obtained was ethyl acetoacetate, b. p. 72-73° (14 mm); $n^{20}D$ 1.4205. Data in the literature [5]: b. p. 74° (14 mm); $n^{20}D$ 1.4197. Found: C 55.36, 55.27; H 7.82, 7.72%. $C_6H_{10}O_3$. Calculated: C 55.40; H 7.68%.

Reaction of methyl-β,β-dichlorovinyl ketone with sodium methylate. To 100 ml of absolute methanol was added 5 g (0.21 M) of metallic sodium. After complete solution of sodium, 30 g (0.22 M) of methyl-β,β-dichlorovinyl ketone was added dropwise to the sodium methylate solution obtained. The reaction mixture was treated as described above. On vacuum distillation, the following fractions were obtained: I with b. p. 56-57° (15 mm); $n^{19}D$ 1.4960; 15 g (initial methyl-β,β-dichlorovinyl ketone); II with b. p. 116-117° (12 mm); $n^{19}D$ 1.4900; 12 g (dimethyl acetal of acetylketene). After redistillation, b. p. was 114.5-115° (11 mm); $n^{19}D$ 1.4915. Found: C 55.19, 55.32; H 7.62, 7.63%. $C_6H_{10}O_3$. Calculated: C 55.40; H 7.69%. The dimethyl acetal of acetylketene was a colorless liquid with a pleasant ethereal odor, stable on storage at 0°.

Reaction of methyl-β,β-dichlorovinyl ketone with sodium benzenesulfinate. 13.9 g (0.1 M) of methyl-β,β-dichlorovinyl ketone was added dropwise, with heating on a water bath and stirring, to a suspension of 14.2 g (0.1 M) of benzenesulfinic acid and 17 g (0.2 M) of sodium bicarbonate in 150 ml of ethanol. After several minutes the mixture took on an intense yellow color, then became dark-red. After 15 minutes the mixture was filtered from the mineral precipitate. On partial evaporation of the alcoholic filtrate, a crystalline precipitate of di-(phenylsulfonyl) methane separated out; weight 10 g. After recrystallizing from ethanol, m. p. was 121-122°. Data in the literature [9]: m. p. 121-122°. Found: C 52.32, 52.44; H 4.10, 4.08; S 21.49, 21.58%. $C_{13}H_{12}O_4S_2$. Calculated: C 52.70; H 4.05; S 21.64%. No melting point depression was observed on mixing a sample with an authentic sample of diphenylsulfonylmethane.

The oil remaining after complete evaporation of alcohol was extracted with ether. The ethereal layer was dried over sodium sulfate, ether evaporated off, and the residue distilled in vacuo. The following fractions were collected: I with b. p. 56-57° (14 mm); 4 g (initial methyl-β,β-dichlorovinyl ketone). Data in the literature [4]: b. p. 58° (14 mm); II with b. p. 158-160° (15 mm); m. p. 79-80°; $n^{19}D$ 1.5720 (1-chloro-1-phenylsulfonylbutenone-3). On distillation, the substance largely decomposed, with evolution of hydrogen chloride and resinification.

In pure form, 1-chloro-1-phenylsulfonylbutenone-3 was a yellow, crystalline substance, readily soluble in alcohol and acetone. Found: C 49.51, 49.34; H 3.62, 3.61; Cl 14.29, 14.40%. $C_{10}H_9ClO_3S$. Calculated: C 49.10; H 3.67; Cl 14.49%.

Reaction of methyl-β,β-dichlorovinyl ketone with sodium thioacetate. 17 g (0.2 M) of sodium bicarbonate was gradually added to a solution of 7.6 g (0.1 M) of thioacetic acid in 50 ml of methanol. Intense evolution of carbon dioxide was observed. 13.9 g (0.1 M) of methyl-β,β-dichlorovinyl ketone was added dropwise to the mixture with constant stirring. The reaction mixture evolved considerable heat, and an intense mercaptan odor was observed. The solution took on a dark-red color. The precipitate separating out after 20 minutes was filtered off and washed free of sodium chloride with several amounts of water. A yellow organic compound remained; weight 13 g. After recrystallizing from methanol, m. p. was 186-187°. According to analytical data, the empirical formula C_4H_4OS· was applicable to the substance. It probably had the structure of a dimer of acetylthioketene. Found: C 47.80, 47.87; H 3.63, 3.75; S 31.86, 31.75%. C_4H_4OS. Calculated: C 48.00; H 3.99; S 32.00%.

After evaporation of the alcoholic filtrate, an oil remained, and was extracted with ether. The ethereal layer was dried over sodium sulfate, ether evaporated off, and the residue distilled in vacuo. Four g of initial methyl-β,β-dichlorovinyl ketone was obtained. A resinous residue remained in the flask.

Reaction of methyl-β,β-dichlorovinyl ketone with potassium thiocyanate. A solution of 9.7 g (0.1 M) of potassium thiocyanate in 100 ml of methanol was added dropwise with stirring and heating on a water bath to 13.9 g (0.1 M) of methyl-β,β-dichlorovinyl ketone. The solution took on a red color. Sodium chloride precipitated out. On cooling, the solution was filtered from the mineral precipitate, alcohol evaporated off, a mixture of oil and crystals remaining. The crystalline substance was again filtered off; weight 13 g. After recrystallizing from ethanol, m. p. was 58-60°. After two recrystallizations from ethanol and chromatography on silicon dioxide, the substance was separated into two different compounds: I with m. p. 64-65° (1-chloro-1-rhodanidebutenone-3). The substance decomposed on storage Found: C 37.24, 37.41; H 2.86, 2.81%. C_5H_4ClOSN. Calculated: C 37.17; H 2.58%; II with m. p. 100-101° (methyl-β,β-dirhodanidevinyl ketone). Found: C 38.70, 39.12; H 2.02, 2.17; N 15.48, 15.47%. $C_6H_4ON_2S_2$. Calculated: C 39.12; H 2.17; N 15.20%.

SUMMARY

A study was made of the reaction of methyl-β,β-dichlorovinyl ketone with a series of nucleophilic reagents (sodium alcoholates, amines, salts of carboxylic, benzosulfinic, and thioacetic acids, potassium thiocyanate, bromide, and cyanide).

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SYNTHESIS OF ORGANOANTIMONY COMPOUNDS VIA DIARYLIODONIUM SALTS

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It has been shown by us previously [1] that double diaryliodonium salts, similarly to double diazonium salts, are decomposed by metallic powders with formation of organometallic compounds. Instead of using double iodonium salts alone, a mixture diaryliodonium chloride and the chloride of a metal can be used successfully. In particular, on this has been based a method for synthesis of organotin [1, 2], and organobismuth [3] compounds. Organomercury compounds [4] are prepared by decomposing with mercury double diaryliodonium salts with mercuric chloride and also diaryliodonium chlorides.

In the present work the method for iodonium salts was extended to the synthesis of organoantimony compounds. To determine optimum conditions, we carried out decomposition of the double salt of diphenyliodonium chloride and antimony trichloride, and of a mixture of $(C_6H_5)_2ICl$ and $SbCl_3$.

We used the double salt $[(C_6H_5)_2ICl]_2 \cdot SbCl_3$, which was prepared by mixing hydrochloric acid solutions of diphenyliodonium chloride and antimony trichloride, and had the composition indicated independently of the proportion of initial components. Decomposition of the double salt $[(C_6H_5)_2ICl]_2 \cdot SbCl_3$ was achieved with antimony powder in acetone and ethyl acetate at different temperatures and with various proportions of the reagents. Results of these experiments are given in Table 1.

TABLE 1. Decomposition of $[(C_6H_5)_2ICl]_2 \cdot SbCl_3$ by Antimony Powder under Different Conditions

Molecular ratio of double salt and antimony	Reaction conditions	Reaction time, hours	Total yield* of organoantimony compounds, %
1:1.6	In acetone at room temperature	25	15
1:4.8	The same	55	33
1:3.0	In boiling acetone	3	63
1:4.8	In ethyl acetate at room temperature	55	38
1:4.8	In boiling ethyl acetate	6	22
1:4.8	The same	12	27

* Yield in all cases calculated on double iodonium salt used in the reaction.

From Table 1 it is seen that at room temperature the reaction proceeds slowly both in acetone and in ethyl acetate independently of the amount of antimony used in decomposition. The most suitable solvent is boiling acetone, in which the reaction is practically complete after 3 hr, total yield of organoantimony compounds then amounting to 63%.

It should be noted that on decomposing double iodonium salts with antimony powder, as in decomposition of double diazonium salts, a mixture of organoantimony compounds is obtained, the formation of which can be represented by the following equations:

$$9\,[(C_6H_5)_2ICl]_2\cdot SbCl_3+8Sb\rightarrow 6\,(C_6H_5)_3SbCl_2+18C_6H_5I+11SbCl_3$$

$$3\,[(C_6H_5)_2ICl]_2\cdot SbCl_3+2Sb\rightarrow 3\,(C_6H_5)_2SbCl_3+6C_6H_5I-2SbCl_3$$

$$3\,[(C_6H_5)_2ICl]_2\cdot SbCl_3+4Sb\rightarrow 3\,(C_6H_5)_2SbCl+6C_6H_5I+4SbCl_3$$

The basic disadvantage in the method described is the necessity of obtaining double iodonium salts, which in many cases are substances difficult to prepare owing to poor solubility of many diaryliodonium chlorides in hydrochloric acid. In particular, this applies to iodonium salts containing a halogen in the aromatic nucleus.

We found previously that double iodonium salts of chlorides of tin [1], bismuth [3], and mercury [4] can be successfully decomposed with a mixture of diaryliodonium chloride and a metallic chloride. In the present work it is shown that on decomposing a mixture of $(C_6H_5)_2ICl$ and $SbCl_3$ with antimony powder in boiling acetone, organoantimony compounds are formed with the same yield as in decomposition of the double salt $[(C_6H_5)_2ICl]_2\cdot SbCl_3$. Decomposition of a mixture of Ar_2ICl and $SbCl_3$ with antimony in boiling acetone has been extended by us to synthesis of organoantimony compounds with other radicals. In Table 2 are shown the diaryliodonium salts and yields of organoantimony compounds formed. As seen from Table 2, decomposition of diaryliodonium chlorides with antimony in presence of $SbCl_3$ results in a mixture of organoantimony compounds in adequate total yield (60-70%). It is noted in this case also that organoantimony compounds are evidently obtained as a result of decomposition of double diaryliodonium salts of antimony trichloride. This is indicated by the fact that on boiling a mixture of $(C_6H_5)_2ICl$ and $SbCl_3$ in acetone in absence of antimony powder we obtained from the acetone solution only a double salt, the results of the analysis of which correspond to the composition: $[(C_6H_5)_2ICl]_{1.8}\cdot SbCl_3$. Most probably, the substance obtained by us was a mixture of the two double iodonium salts $(C_6H_5)_2ICl\cdot SbCl_3$ and $[(C_6H_5)_2ICl]_2\cdot SbCl_3$.

TABLE 2. Decomposition of a Mixture of Ar_2ICl and $SbCl_3$ with Antimony Powder in Boiling Acetone

Iodonium salt	Yield of organoantimony compounds, %			
	Ar_2SbX	Ar_2SbX_3	Ar_3SbX_2	total yield
$(C_6H_5)_2ICl$	20	41	–	61
$(p\text{-}ClC_6H_4)_2ICl$	15	11	43	69
$(p\text{-}BrC_6H_4)_2ICl$	42	17	18	61.7
$(p\text{-}CH_3C_6H_4)_2ICl$	22	29	8.5	59.5

However, if formation of organoantimony compounds on decomposing a mixture of Ar_2ICl and $SbCl_3$ proceeds via a double iodonium salt stage, we should be interested in clarifying the question as to whether organometallic antimony compounds would be obtained on reacting a diaryliodonium chloride with antimony powder in absence of antimony trichloride. It should be noted that Sandin with co-workers [5] decomposed $(C_6H_5)_2ICl$ with antimony in aqueous solution in presence of Na_2S, obtaining triphenylantimony sulfide, the yield of which they do not indicate. We found that the reaction between diphenyliodonium chloride and antimony in acetone leads to formation of organoantimony compounds, the yield of the latter depending to a large degree, however, on the form of the antimony used. Thus, using a powder of finely divided metallic antimony, total yield of organoantimony compounds amounts to 28%. Almost the same yield (24%) is achieved by using antimony prepared in the following manner. To a solution of $SbCl_3$ in dilute hydrochloric acid was added an equimolecular amount of zinc powder; the precipitate settling out was filtered off, washed with dilute hydrochloric acid, water, soda solution (to remove possible traces of HCl), again with water, alcohol and ether, then air-dried.

If antimony prepared in the manner described above is used, and washing with soda solution is omitted (i.e., possible traces of acid are not removed), yield of organoantimony compounds amounts to 50%. Practically the same yield* (52%) is achieved on decomposing $(C_6H_5)_2ICl$ with finely divided antimony powder in presence of traces of hydrochloric acid. The data obtained shows that hydrochloric acid promotes formation of organoantimony compounds in decomposition of $(C_6H_5)_2ICl$ with antimony. The role of HCl evidently consists of forming $SbCl_3$ (in acetone solution antimony reacts with HCl). From this it is seen that decomposition of diphenyliodonium chloride with antimony leads to organoantimony compounds, antimony trichloride promoting this reaction.

* This fact was confirmed in 4 parallel experiments.

In conclusion, it is noted that use of diphenyliodonium iodide instead of the chloride leads to a marked lowering of yield (9% as against 50%) of oganoantimony compounds.

EXPERIMENTAL

Decomposition of double salt $[(C_6H_5)_2Cl]_2 \cdot SbCl_3$ with antimony powder. a) 17 g (0.02 M) of the double salt $[(C_6H_5)_2ICl]_2 \cdot SbCl_3$ in 200 ml of anhydrous boiling acetone was decomposed with 7.3 g (0.06 g-at) of freshly reduced antimony powder by stirring for 3 hr. The inorganic precipitate was filtered off, washed with acetone, and the solvent distilled off. The product remaining after solvent distillation was dissolved in 35 ml of benzene and extracted twice with 5 N hydrochloric acid to remove inorganic antimony compounds. Benzene was distilled off, and alcohol added to the residue. On cooling the alcoholic solution, no triaryl compounds of antimony precipitated. The alcoholic solution was poured into 5% ammonia solution. The precipitate settling out was filtered off, washed with water, a small amount of alcohol, and thoroughly washed with ether. The diphenylstibinic acid remaining after washing with ether was dissolved in glacial acetic acid and reprecipitated with 5% ammonia solution. Yield of diphenylstibinic acid was 2.4 g (31%).

For identification, the diphenylstibinic acid was converted into diephenylantimony trichloride by boiling with 5 N hydrochloric acid; m. p. 175-176°. Data in the literature [6]: m. p. 176°.

The oil remaining after ether evaporation was treated with boiling glacial acetic acid, 2 g (32%) of $(C_6H_5)_3 \cdot Sb(OCOCH_3)_2$ being obtained; m. p. 210°. Data in the literature [7]: m. p. 215°. On boiling with alcoholic HCl solution, the triphenylantimony diacetate obtained was converted into triphenylantimony dichloride; m. p. 141-142.5°. Data in the literature [8]: m. p. 141.5°; [9]: 142°. A sample mixed with authentic triphenylantimony dichloride gave no melting point depression.

b) 5 g (0.006 M) of the double salt $[(C_6H_5)_2ICl]_2 \cdot SbCl_3$ was decomposed with 3.4 g (0.028 g-at) of antimony powder in 15 ml of anhydrous acetone by stirring for 55 hr. As a result of further treatment similar to that in the preceeding experiment, from the alcoholic solution triphenylantimony dichloride was obtained, yield 0.08 g (4%); m. p. 141°. Data in the literature [8]: m. p. 141.5°. In addition, 0.35 g (19.5%) of diphenylstibinic acid was obtained, also 0.2 g (10%) of diphenylstibine acetate with m. p. 128°. Data in the literature [10]: m. p. 132°. A sample mixed with authentic diphenylsibine acetate gave no melting point depression.

Decomposition of diphenyliodonium chloride with antimony powder in presence of antimony trichloride. A mixture of 19 g (0.06 M) of diphenyliodonium chloride and 7 g (0.03 M) antimony trichloride in 200 ml of anhydrous acetone was boiled with 17 g (0.14 g-at) of freshly reduced antimony by mixing for 3 hr. The inorganic precipitate was then filtered off, and the filtrate subjected to the usual treatment. As a result, 3.8 g (41%) of diphenylstibinic acid and 2 g (20%) of diphenylstibine acetate were obtained; m. p. 130-132°. Data in the literature [10]: m. p. 132°.

The diphenylstibinic acid was identified as diphenylantimony trichloride; m. p. 175.5°. Data in the literature [7]: m. p. 175°; [6]: m. p. 176°.

Decomposition of di-(p-chlorophenyl)iodonium chloride with antimony powder in presence of antimony trichloride. A mixture of 7.7 g (0.02 M) of di-(p-chlorophenyl)iodonium chloride and 2.3 g (0.01 M) of antimony trichloride in 20 ml of anhydrous acetone was boiled with 3.7 g (0.03 g-at) of freshly reduced antimony by stirring for 3 hr. The inorganic precipitate was filtered off, and the solvent evaporated. The remainder was dissolved in benzene; the benzene solution was washed several times with 5 N hydrochloric acid. Benzene was evaporated, and ethyl alcohol added to the residue. On cooling the alcoholic solution, tri-(p-chlorophenyl) antimony dichloride was obtained; yield 1.5 g (43%); m. p. 192°. Data in the literature [11]: m. p. 193°.

The alcoholic filtrate was treated in the following manner. Most of the alcohol was distilled off, then p-chloroiodobenzene formed on decomposition of the iodonium salt was removed by steam-distillation. The residue remaining in the distillation flask was filtered off, washed with a small amount of alcohol and thoroughly washed with ether. The remaining di-(p-chlorophenyl)stibinic acid was dissolved in acetic acid and precipitated with ammonia; yield 0.4 g (11%). By boiling with 5 N hydrochloric acid, the di-(p-chlorophenyl)stibinic acid was converted into di-(p-chlorophenyl)antimony trichloride; m. p. 150°. Data in the literature [12]: m. p. 149-150°.

From the ethereal solution after solvent evaporation and heating the residue with glacial acetic acid, di-(p-chlorophenyl)stibine acetate was obtained, and was recrystallized from acetic acid; yield 0.6 g (15%); m. p. 127-128°. Data in the literature [10]: m. p. 126°.

Decomposition of di-(p-bromophenyl)iodonium chloride with antimony powder in presence of antimony trichloride. A mixture of 2.4 g (0.005 M) of di-(p-bromophenyl)iodonium chloride and 0.6 g (0.0026 M) of antimony trichloride in 20 ml of anhydrous acetone was boiled with 0.9 g (0.0074 g-at) of freshly reduced antimony by stirring for 3 hr. As a result of treatment similar to that in the preceeding experiment, 0.2 g (18%) of tri-(p-bromophenyl)-antimony dichloride was obtained; m. p. 194°. Data in the literature [10]: m. p. 198°. Found: C 32.99; H 1.97%. $C_{18}H_{12}Br_3Cl_2Sb$. Calculated: C 32.72; H 1.83%.

On pouring the alcoholic solution into ammonia, 0.02 g (1.7%) of di-(p-bromophenyl)stibinic acid and di-(p-bromophenyl)stibine oxide were obtained. By boiling with 5 N hydrochloric acid, the di-(p-bromophenyl)stibinic acid was converted into di-(p-bromophenyl)antimony trichloride; m. p. 159°. Data in the literature [12]: m. p. 159°. Found: C 26.97, 26.87; H 1.81, 1.84%. $C_{12}H_8Br_2Cl_3Sb$. Calculated: C 26.68; H 1.49%.

The di-(p-bromophenyl)stibine oxide was converted into di-(p-bromophenyl)stibine acetate by heating with acetic acid; yield 0.5 g (42%); m. p. 129°. Data in the literature [10]: m. p. 131-132°.

Decomposition of di-(p-tolyl)iodonium chloride with antimony powder in presence of antimony trichloride. A mixture of 6.9 g (0.02 M) of di-(p-tolyl)iodonium chloride and 2.3 g (0.01 M) of antimony trichloride in 40 ml of anhydrous acetone was boiled with 3.7 g (0.03 g-at) of freshly reduced antimony with stirring for 3 hr. After filtering off the inorganic precipitate and the usual treatment of the reaction mixture, 0.32 g (8.5%) of tri-(p-tolyl)-antimony dichloride was obtained; m. p. 157°. Data in the literature [12]: m. p. 156-157°. One g (29%) of di-(p-tolyl)stibinic acid was obtained; the acid was identified as di-(p-tolyl)antimony trichloride; m. p. 147°. Data in the literature [13]: m. p. 141-142°; [14] m. p. 155°. Found: C 40.57, 40.60; H 3.75, 3.90%. $C_{14}H_{14}Cl_3Sb$. Calculated: C 40.97; H 3.44%. In addition, 0.8 g (22%) of di-(p-tolyl)stibine acetate was obtained with m. p. 119°. Data in the literature [15]: m. p. 122-123°.

Decomposition of diphenyliodonium chloride with antimony powder. 6.3 g (0.02 M) of diphenyliodonium chloride was decomposed with 3.7 g (0.03 g-at) of freshly reduced antimony in 40 ml of boiling acetone by stirring for 3 hr. On completion of the reaction, the inorganic precipitate was filtered off, acetone distilled off, and the remainder dissolved in benzene. The benzene solution was washed several times with 5 N hydrochloric acid. Benzene was evaporated off, and alcohol added to the residue. On cooling the alcoholic solution, triphenylantimony dichloride precipitated; yield 0.75 g (26%); m. p. 142°. Data in the literature [10]: m. p. 143°.

The alcoholic filtrate was poured into 5% ammonia solution, the precipitate separating out filtered off, washed with water, a small amount of alcohol, and then thoroughly with ether. After washing with ether, diphenylstibinic acid remained; yield 0.26 g (8%). The diphenylstibinic acid was identified as diphenylantimony trichloride; m. p. 178°. Data in the literature [6]: m. p. 176°.

After evaporation of ether, an oil remained, which was treated with glacial acetic acid. On cooling, crystals of $(C_6H_5)_3Sb(OH)(OCOCH_3)$ precipitated; yield 0.1 g (4%); m. p. 188°. Found: C 56.30, 56.44; H 4.50, 4.55%. $C_{20}H_{19}O_3Sb$. Calculated: C 56.00; H 4.46%.

On adding petroleum ether to the acetic filtrate, diphenylstibine acetate precipitated; yield 0.85 g (25%); m. p. 128°. Data in the literature [10]: m. p. 132°.

Decomposition of diphenyliodonium iodide. To prepare diphenyliodonium iodide, 11 g (0.034 M) of diphenyliodonium chloride was dissolved in hot methyl alcohol. To the resulting solution was added a solution of 6 g (0.036 M) of potassium iodide in a water – methyl alcohol mixture (1:2). The precipitate settling out was filtered off, and washed with water and ether; yield was quantitative, m. p. 162°. Found: C 35.11; H 2.64%. $C_{12}H_{10}I_2$. Calculated: C 35.32; H 2.47%.

8.2 g (0.02 M) of diphenyliodonium iodide was decomposed with 3.7 g (0.03 g-at) of freshly reduced antimony under the conditions of the preceeding experiment. As a result of the usual treatment, 0.2 g (9%) of diphenylstibinic acid and 3.8 g of iodobenzene were obtained.

SUMMARY

1. A study was made of the decomposition of diaryliodonium salts with antimony powder under various conditions.

2. A method was evolved for synthesis of organoantimony compounds, consisting of decomposing mixture of a diaryliodonium chloride and $SbCl_3$ with antimony powder in boiling acetone.

3. On changing from diphenyliodonium chloride to diphenyliodonium iodide, yield of organoantimony compounds was lowered markedly.

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ORGANOPHOSPHOROUS MONOMERS

COMMUNICATION 2. α-CHLORO- AND α-BROMOVINYLPHOSPHINIC ACIDS AND THEIR DERIVATIVES

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In a previous communication in this series [1] we showed that the di-acid chloride of vinylphosphinic acid, $CH_2=CHPOCl_2$, can be readily prepared by catalytic dehydrochlorination of the di-acid chloride of β-chloroethylphosphinic acid. There also was given the information that the di-acid chloride of vinylphosphinic acid can be widely used in synthesis of organophosphorus monomers and polymers. In the present article are given results obtained in bromination and chlorination of the di-acid chloride of vinylphosphinic acid.

Addition of bromine to the di-acid chloride of vinylphosphinic acid is carried out as simply as to its ethyl ester [1, 2]. The reaction is complete after standing for 24 hr at room temperature a mixture of equimolecular amounts of the acid chloride and bromine in solution in chloroform

$$CH_2=CHPOCl_2 + Br_2 \rightarrow BrCH_2CHBrPOCl_2$$

The di-acid chloride of α,β-dibromoethylphosphinic acid (I) obtained in this manner was hydrolyzed to the free acid (II), the aniline salt of which (III) melted at 194-195°. During an attempt to prepare the anilide of this acid, dehydrobromination of the substance took place and the dianilide of α-bromovinylphosphinic acid (VIII) was obtained.

$BrCH_2CHBrPOX_2$

(I) X=Cl
(II) X=OH
(III) X=OH (aniline salt)

$CH_2=CBrPOX_2$

(IV) X=Cl
(V) X=OH
(VI) X=OH (aniline salt)
(VII) $X=OC_2H_5$
(VIII) $X=NHC_6H_5$

Under conditions similar to those previously found necessary by us for dehydrochlorination of the di-acid chloride of β-chloroethylphosphinic acid, dehydrobromination of the di-acid chloride of α,β-dibromoethylphosphinic acid was achieved:

$$BrCH_2CHBrPOCl_2 \xrightarrow[-HBr]{BaCl_2} CH_2=CBrPOCl_2$$

At the same time, the acid chloride of α-bromovinylphosphinic acid (IV) was formed in ~80% yield. By hydrolysis of the acid chloride, acid (V) was obtained as a syrup; the aniline salt of the acid, (VI), melts at 187-188°.

By reacting this acid chloride with alcohol, the ethyl ester of α-bromovinylphosphinic acid (VII) was obtained, synthesized previously by another method [1]. Its structure was demonstrated by ozonization; on ozonization, the dimedon derivative of formaldehyde was obtained.

Reaction of the di-acid chloride of vinylphosphinic acid with chlorine proceeds with considerably greater difficulty than with bromine. At room temperature, chlorine is added to the acid chloride very slowly; the reaction is accelerated somewhat by the action of sunlight. On heating the reaction mixture in a sealed tube at 125-130° for 5 hr, yield of reaction products reaches about 80%. In this case, besides chlorine addition at the double bond and formation of the di-acid chloride of α,β-dichloroethylphosphinic acid (IX), hydrogen chloride is split off from the

latter, the di-acid chloride of α-chlorovinylphosphinic acid (X) being formed simultaneously. Both acid chlorides were obtained in pure form. It is noticed that the experiment to obtain the acid chloride of α,β-dichloroethylphosphinic acid by oxidative phosphorylation of vinyl chloride described in the literature [3] led to a mixture of isomers, separation of which was not achieved.

(IX) $ClCH_2CHClPOCl_2$ $CH_2=CClPOX_2$
(X) X=Cl; (XI) X=OH
(XII) X=OH (aniline salt) (XIII) $X=OCH_3$
(XIV) $X=OC_2H_5$; (XV) $X=NHC_6H_5$

The di-acid chloride of α,β-dichloroethylphosphinic acid was converted by catalytic dehydrochlorination over barium chloride into the acid chloride of α-chlorovinylphosphinic acid. As shown in further experiments, dehydrochlorination of the acid chloride of α,β-dichloroethylphosphinic acid can be achieved both in the absence of catalyst and at a lower temperature. Thus, if the reaction mixture formed by chlorination of the di-acid chloride of vinylphosphinic acid is maintained prior to the onset of distillation at 150-155° until hydrogen chloride evolution ceases, then distillation results mainly in formation of the di-acid chloride of α-chlorovinylphosphinic acid and only a small amount of the di-acid chloride of α,β-dichloroethylphosphinic acid. Much the same result is obtained on heating the reaction mixture in a sealed tube at 140-150°.

By reacting the acid chloride of α-chlorovinylphosphinic acid with the alcohols, the methyl (XIII) and ethyl (XIV) esters of α-chlorovinylphosphinic acid are obtained. On reacting with aniline, the dianilide of the same acid is obtained (XV).

EXPERIMENTAL

Di-acid chloride of α,β-dibromoethylphosphinic acid (I). 10.8 g (0.075 M) of the di-acid chloride of vinylphosphinic acid and 11.12 g (0.07 M) of bromine in 50 ml of chloroform were left overnight at room temperature. After distillation in a stream of carbon dioxide, a substance was obtained with b. p. 120-122° (5 mm); yield 14.3 g (62.5%); $n^{20}D$ 1.5698; d^{20}_4 2.2155; MR found 45.07; MR calculated 45.02. On standing, the substance crystallized; m. p. 33-34°. Found: C 7.6; 7.4; H 1.1, 1.2; P 10.2, 9.6; Hal 76.1, 76.1%. $C_2H_3PCl_2Br_2$. Calculated: C 7.9; H 1.0; P 10.2; Hal 75.7%.

α,β-Dibromoethylphosphinic acid (II). To 6 ml of water was gradually added 2 g of the di-acid chloride of α,β-dibromoethylphosphinic acid. After distillation of water the residue was dried over phosphorus pentoxide and alkali. 1.6 g (90.8%) of colorless crystals was obtained with m. p. 115-116°. The substance was readily soluble in water and alcohol, insoluble in organic solvents. Found: C 8.8, 8.8; H 1.9, 2.0; P 11.2, 11.4%. $C_2H_5PO_3Br_2$. Calculated: C 9.0; H 1.9; P 11.6%.

Aniline salt of α,β-dibromoethylphosphinic acid (III). To 2.7 g (0.01 M) of α,β-dibromoethylphosphinic acid in 3 ml of alcohol was added 0.93 g (0.01 M) of aniline; the precipitate settling out was washed with ether and recrystallized from alcohol. 2.5 g (69.5%) of a substance was obtained with m. p. 194-195°. Found: C 26.6, 26.8; H 3.4, 3.3; P 8.6, 8.7; N 4.2, 4.0; Br 44.1, 44.2%. $C_8H_{12}PO_3NBr_2$. Calculated: C 26.6; H 3.3; P 8.6; N 3.9; Br 44.3%.

Dianilide of α-bromovinylphosphinic acid (VIII). 1.35 g (0.0044 M) of the di-acid chloride of α,β-dibromoethylphosphinic acid and 1.64 g (0.0176 M) of aniline in 10 ml of benzene were heated for 1.5 hr on a boiling water bath. After removal of the precipitate, benzene was distilled off, and the residue recrystallized from alcohol. 0.4 g (26.6%) of a substance was obtained with m. p. 156-157°. Found: C 49.6, 49.9; H 4.3, 4.4; P 9.3, 9.1; N 8.3, 8.3%. $C_{14}H_{14}POBrN_2$. Calculated: C 49.9; H 4.2; P 9.2; N 8.3%.

Di-acid chloride of α-bromovinylphosphinic acid (IV). 20 g (0.066 M) of the di-acid chloride of α,β-dibromoethylphosphinic acid was passed through a quartz tube filled with barium chloride and heated to 330-340°. After distillation of the condensate, 11.4 g (77.5%) of a liquid was obtained with b. p. 194-197° at atmospheric pressure; $n^{20}D$ 1.5273; d^{20}_4 1.8393; MR found 37.44; MR calculated 36.79. On standing, the substance crystallized; m. p. 36-39°. Found: C 10.9, 11.0; H 1.2, 1.0; P 14.1, 13.9%. $C_2H_2POCl_2Br$. Calculated: C 10.7; H 0.9; P 13.8%.

Soborovskii with co-workers [4] obtained the di-acid chloride of β-bromovinylphosphinic acid, the constants of which [b. p. 81-82° (3 mm); $n^{20}D$ 1.7415; d^{20}_4 1.4884] differed markedly from the constants of the α-derivative.

α-Bromovinylphosphinic acid (V). Obtained similarly to substance (II) from 2.6 g of the di-acid chloride of α-bromovinylphosphinic acid; a colorless syrup; yield 2.1 g (96%). Found: C 13.0, 13.1; H 2.5, 2.5; P 17.0, 16.9. $C_2H_4PO_3Br$. Calculated: C 12.9; H 2.2; P 16.6%.

Aniline salt of α-bromovinylphosphinic acid (VI). Obtained from 1.3 g (0.007 M) of α-bromovinylphosphinic acid and 0.65 g (0.007 M) of aniline similarly to substance (III); yield 0.7 g (36%); m. p. 187-188°. Found: C 34.4, 34.7; H 4.2, 4.2; P 11.1, 11.2; N 5.5, 5.3%. $C_8H_{11}PO_3NBr$. Calculated: C 34.3; H 4.0; P 11.1; N 5.0%.

Ethyl ester of α-bromovinylphosphinic acid (VII). To 50 ml of absolute ethyl alcohol at 0 – 5° was gradually added with stirring 7 g (0.03 M) of the di-acid chloride of α-bromovinylphosphinic acid. The mixture was then left overnight. After elimination of alcohol, the residue was distilled in vacuo. 4.1 g (54%) of a substance was obtained with b. p. 78-78.5° (2 mm); $n^{20}D$ 1.4649; d^{20}_4 1.3778; MR found 48.74; MR calculated 48.07. Found: C 30.4, 30.3; H 5.2, 5.1; P 12.4, 12.8; Br 32.9, 33.0%. $C_6H_{12}PO_3Br$. Calculated: C 29.6; H 5.0; P 12.7; Br 32.9%.

Ozonization of ethyl ester of α-bromovinylphosphinic acid. Into a solution of 1 g of the ethyl ester of α-bromovinylphosphinic acid in 50 ml of carbon tetrachloride cooled in ice water was bubbled ozonized oxygen for 3 hr. To the solution was added 75 ml of water, and the mixture heated for 9 hr at 60°. From the distillate was obtained the condensation product with dimedon; m. p. 189-190°. Mixed sample: m. p. 189-190°.

Di-acid chloride of α,β-dichloroethylphosphinic acid (IX). A solution of 7.25 g (0.05 M) of the di-acid chloride of vinylphosphinic acid in 15 ml of carbon tetrachloride was saturated with chlorine until increase in weight was 4.1 g (0.058 M). The mixture was then allowed to stand for four days at room temperature. From the reaction mixture two fractions were obtained: I with b. p. 80-87° (8 mm); 3.1 g (34%), being the di-acid chloride of α-chlorovinylphosphinic acid; II with b. p. 84-85° (3 mm); 3.2 g (29.5%), being the di-acid chloride of α,β-dichloroethylphosphinic acid; $n^{20}D$ 1.5220; d^{20}_4 1.6616; MR found 39.62; MR calculated 39.22. Found: C 11.5, 11.5; H 1.3, 1.4; P 14.2, 14.3; Cl 65.8, 65.4%. $C_2H_3Cl_4PO$. Calculated: C 11.1; H 1.4; P 14.3, Cl 65.7%.

Di-acid chloride of α-chlorovinylphosphinic acid (X). 18.3 g (0.084 M) of the di-acid chloride of α,β-dichloroethylphosphinic acid was passed through a tube filled with barium chloride and heated to 330-340°. On distillation of the condensate a substance was obtained with b. p. 61-62° (11 mm) – 13.3 g (87.5%); $n^{20}D$ 1.5003; d^{20}_4 1.5453; MR found 33.89; MR calculated 34.17. On standing, the substance crystallized; m. p. 28-30°. Found: C 13.9, 13.8; H 1.3, 1.3; P 17.3, 17.2; Cl 59.1, 58.9%. $C_2H_2POCl_3$. Calculated: C 13.4; H 1.1; P 17.3; Cl 59.3%.

A mixture of 43.5 g (0.3 M) of the di-acid chloride of vinylphosphinic acid and 120 ml of carbon tetrachloride was saturated with chlorine until increase in weight was 23.3 g (0.33 M), and was heated in sealed glass tubes for 5 hr at 125-130°. After elimination of carbon tetrachloride, the residue was distilled at bath temperature 155-160° and 120 mm, and then fractionated. 1.7 g of a substance was obtained with b. p. 88-96° (9 mm); $n^{20}D$ 1.5173 (contaminated di-acid chloride of α,β-dichloroethylphosphinic acid) and 39.7 g (73.5%) of the di-acid chloride of α-chloroethylphosphinic acid with b. p. 59-61° (14 mm); $n^{20}D$ 1.4993; d^{20}_4 1.5418. The substance crystallized; m. p. 29-30°.

α-Chlorovinylphosphinic acid (XI). Obtained similarly to substance (II), from 4.5 g (0.025 M) of the di-acid chloride of α-chlorovinylphosphinic acid; colorless crystals with m. p. 33-34°; 3.5 g (97%). Found: C 16.8, 16.6; H 3.2, 2.9; P 21.5, 21.5; Cl 24.7, 24.5%. $C_2H_4PO_3Cl$. Calculated: C 16.9; H 2.8; P 21.7; Cl 24.9%.

Aniline salt of α-chlorovinylphosphinic acid (XII). Obtained similarly to substance (III), from 1.5 g (0.105 M) of α-chlorovinylphosphinic acid and 0.98 g (0.105 M) of aniline; yield 1.5 g (71%); m. p. 209-210°. Found: C 41.3, 41.0; H 4.8, 4.8; P 13.4, 13.5; N 6.4, 6.2%. $C_8H_{11}PO_3NCl$. Calculated: C 40.8; H 4.7; P 13.2; N 5.9%.

Methyl ester of α-chlorovinylphosphinic acid (XIII). Obtained in the usual manner from 8.95 g (0.05 M) of the di-acid chloride of α-chlorovinylphosphinic acid, 3.2 g (0.1 M) of methyl alcohol, and 10.1 g (0.01 M) of triethylamine in 180 ml of ether; b. p. 60-61° (3 mm); yield 5.7 g (62%); $n^{20}D$ 1.4506; d^{20}_4 1.2715; MR found 36.08; MR calculated 35.94. Found: C 28.7, 28.5; H 5.0, 4.9; P 17.4, 17.5; Cl 20.4, 20.4%. $C_4H_8PO_3Cl$. Calculated: C 28.2; H 4.7; P 18.2; Cl 20.8%.

Ethyl ester of α-chlorovinylphosphinic acid (XIV). Obtained from 8.95 g (0.05 M) of the di-acid chloride of α-chlorovinylphosphinic acid, 4.6 g (0.1 M) of ethyl alcohol, and 10.1 g (0.1 M) of triethylamine in 180 ml of ether; b. p. 77° (3 mm); yield 5.6 g (56.5%); $n^{20}D$ 1.4462; d^{20}_4 1.1622; MR found 45.59; MR calculated 45.18. Found: C 36.4, 36.6; H 6.4, 6.1; P 15.5, 15.6; Cl 17.5, 17.4%. $C_6H_{12}PO_3Cl$. Calculated: C 36.6; H 6.1; P 15.6; Cl 17.8%.

Ozonization of ethyl ester of α-chlorovinylphosphinic acid. The experiment was carried out as in the case of ozonization of the ethyl ester of α-bromovinylphosphinic acid. The condensation product with dimedon melted at 189-190°; the mixed sample had m. p. 189-190°.

Dianilide of α-chlorovinylphosphinic acid (XV). A mixture of 5.37 g (0.03 M) of the di-acid chloride of α-chlorovinylphosphinic acid and 11.16 g (0.12 M) of aniline in 25 ml of benzene was heated for 1.5 hr on a boiling water bath. The precipitate settling out was separated, washed with water to remove aniline hydrochloride and recrystallized from aqueous alcohol. 5.45 g (62%) of acicular crystals was obtained with m. p. 167-169°. Found: C 57.4, 57.3; H 5.1, 5.2; P 10.5, 10.6; Cl 12.3, 12.6%. $C_{14}H_{14}POClN_2$. Calculated: C 57.4; H 4.8; P 10.6; Cl 12.1%.

SUMMARY

By addition of bromine or chlorine to the di-acid chloride of vinylphosphinic acid with subsequent dehydrohalogenation of the reaction products, the di-acid chlorides of α-bromo or α-chlorovinylphosphinic acid can be readily obtained. Several derivatives of these acids were prepared.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

AN INVESTIGATION IN THE FIELD OF THE UNSATURATED PHOSPHINIC ACIDS

COMMUNICATION 23. ADDITION OF PHOSPHORUS PENTACHLORIDE TO ETHYNYLCYCLOHEXENE-1

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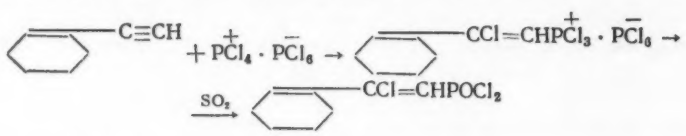
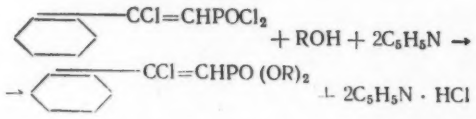
Original article submitted July 23, 1959

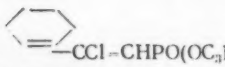
Continuing our work in the field of derivatives of unsaturated phosphinic acids, in the present communication we describe the addition of phosphorus pentachloride to ethynylcyclohexene-1.



The resulting acid chloride readily reacts with alcohols.



By this reaction [1], we have prepared the ethyl and n-propyl esters of β,β'-cyclohexenylchlorovinylphosphinic acid. Constants of the compounds obtained are given in the table.

Formula	B.p., °C mm Hg	$n^{20}D$	d^{20}_4	Yield, %	MR found	MR calcd.	C=C cm^{-1}	P=O cm^{-1}
Acid chloride of β,β'-cyclohexenylchlorovinylphosphinic acid	132 (2)	1.5808	1.4103	54	61.35	58.93	1620 med. 1558 v.s.	1275 v.s.
Diethyl ester of β,β'-cyclohexenylchlorovinylphosphinic acid	132 (1)	1.5142	1.1688	90.5	71.98	70.204	1625 s. 1570 s.	1260 v.s.
 Di-n-propyl ester of β,β'-cyclohexenylchlorovinylphosphinic acid	131 (1)	1.5083	1.1235	56	71.38	79.44	1625 s. 1570 s.	1260 v.s.

With the aim of studying their structure, the infrared spectra of the acid chloride (Fig. 1) and the esters of β,β'-cyclohexenylchlorovinylphosphinic acid (Fig. 2) were measured. Frequencies serving as a basis for analysis of infrared spectra are shown in the table.

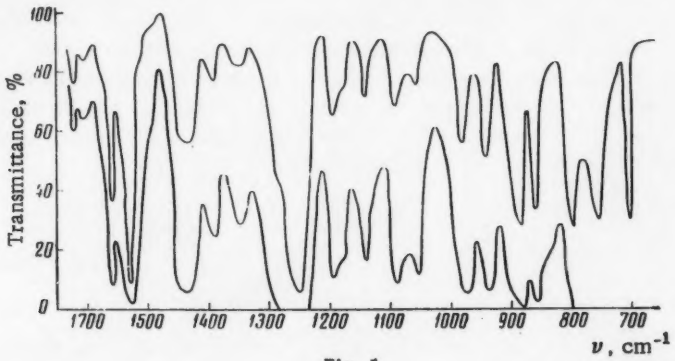


Fig. 1

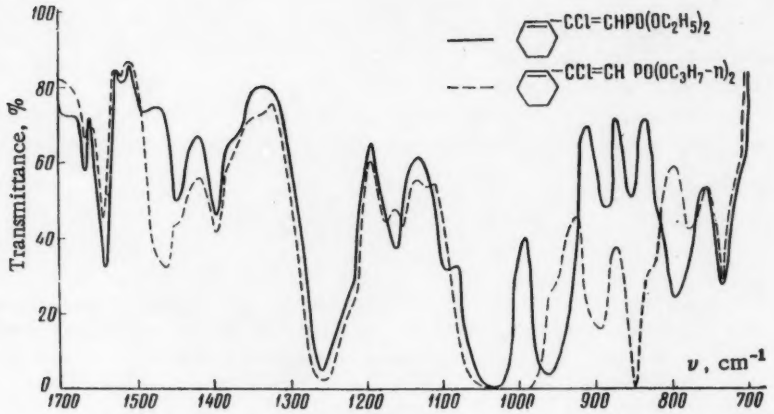


Fig. 2

In the region of valence vibrations of the C=C bond in the spectrum of our compounds there are two bands 1625, 1620 cm^{-1} and 1570, 1558 cm^{-1}, which confirms the presence in the molecules of a conjugated system of double bonds [2, 3]. Absorption bands 1275, 1260 cm^{-1} are valence vibrations of P=O bonds [4, 5].

EXPERIMENTAL

Acid chloride of β,β'-cyclohexenylchlorovinylphosphinic acid. To a solution of 83.3 g (0.4 M) of phosphorus pentachloride in 150 ml of absolute benzene was added with stirring 21.2 g (0.2 M) of ethynylcyclohexene-1. Further treatment of the product was carried out according to the method described previously [6]. 26.0 g of acid chloride was obtained; yield 54%; b. p. 132° (2 mm); $n^{20}D$ 1.5808; d^{20}_4 1.4103; MR found 61.35; MR calculated 58.93; mol. wt. 259.5. Found: C 36.91, 36.69; H 3.96, 3.93; Cl 41.38, 41.38; P 12.05, 11.73%. $C_8H_6POCl_3$. Calculated: C 37.00; H 3.85; Cl 41.08; P 11.96%.

Esters of β,β'-cyclohexenyl-1-chlorovinylphosphinic acid. To prepare the diethyl ester, to a solution of 4.6 g (0.1 M) of absolute ethyl alcohol and 7.9 g (0.1 M) of absolute pyridine in 100 ml of absolute benzene was added with stirring 12.98 g (0.05 M) of the acid chloride of β,β'-cyclohexenyl-1-chlorovinylphosphinic acid. As a result of the reaction, 12.6 g (90.5% theoretical) of the diethyl ester of β,β'-cyclohexenyl-1-chlorovinylphosphinic acid was obtained. Constants: b. p. 132° (2 mm); $n^{20}D$ 1.5142; d^{20}_4 1.1688. MR found 71.98; MR calculated 70.20. Found:

C 50.90, 50.84; H 7.04, 7.05; P 11.44, 11.18%. $C_{12}H_{16}PO_3Cl$. Calculated: C 50.50; H 7.18; P 11.27%. On mixing the substance in the same molar proportions with n-propynyl alcohol* 7.9 g (56% theoretical) of the n-propyl ester of β,β'-cyclohexenyl-1-chlorovinylphosphinic acid was obtained with b. p. 131°; $n^{20}D$ 1.5083; d^{20}_4 1.123; MR found 81.38; MR calculated 79.44. Found: P 10.01, 9.78; Cl 11.07, 11.34%. $C_{14}H_2OPOCl_3$. Calculated: P 10.104; Cl 11.57%.

Measurement of infrared spectra. Measurement of absorption spectra in the infrared region was carried out on a Hilger (model 209) infrared spectrometer, using the single beam variant of this model. A Nernst Lamp was used as the light source. Measurements in the region from 4.0 to 15 μ were carried out with a rock salt prism. Rock salt plates were used as cells. Layer thickness of the substance being investigated was regulated with aluminum foil packing and was 10.30 and 70 μ. Accuracy in determination of position of maxima of the absorption bands was 2 cm^{-1}.

SUMMARY

1. The acid chloride of β,β'-cyclohexenyl-1-chlorovinylphosphinic acid was prepared.
2. The diethyl and di-n-propyl esters of β,β'-cyclohexenyl-1-chlorovinylphosphinic acid were synthesized.
3. The structure of the substances obtained was studied with the help of infrared spectroscopy.

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* Publishers note: n-propynyl alcohol, although indicated as such in the Russian, is probably n-propyl alcohol.

AN INVESTIGATION IN THE FIELD OF THE DERIVATIVES OF UNSATURATED PHOSPHINIC ACIDS

COMMUNICATION 24. REACTION OF PHOSPHORUS PENTACHLORIDE WITH ALKOXYACETYLENES

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In developing the work on addition of phosphorus pentachloride to unsaturated compounds, we began an investigation of the addition of phosphorus pentachloride to alkoxyacetylenes. In the present work is described the addition of phosphorus pentachloride to 5-phenoxypentyne-1 and 5-ethoxypentyne-1. By subsequent treatment of the addition products with sulfur dioxide, the acid chlorides of 2-chloro-5-phenoxypentene-1-phosphinic acid and 2-chloro-5-ethoxypentene-1-phosphinic acid respectively are obtained

$$RO(CH_2)_3C{\equiv}CH + 2PCl_4^+PCl_6^- \rightarrow RO(CH_2)_3CCl{=}CHPCl_3^+PCl_6^- \xrightarrow{SO_2} \rightarrow RO(CH_2)_3CCl{=}CHPOCl_2 + POCl_3 + SOCl_2$$

From the acid chloride of 2-chloro-5-phenoxypentene-1-phosphinic acid were obtained by the usual method [1] the dimethyl, diethyl, and dibutyl esters. The corresponding acid was obtained by hydrolysis of the acid chloride. The diethyl ester was obtained from the acid chloride of 2-chloro-5-ethoxypentene-1-phosphinic acid. The compounds synthesized, their constants and analysis are shown in Table 1.

The IR -spectra were taken of the diethyl and dibutyl esters of 2-chloro-5-phenoxypentene-1-phosphinic acid (Figs. 1 and 2).* For compounds containing one isolated double bond, the presence of an absorption band in the range 1680-1620 cm^{-1} is characteristic. In our case, for $C_6H_5O(CH_2)_3CCl = CHPO(OR)_2$ the absorption band lies in the region 1580 cm^{-1}. Such a displacement can be explained by the influence of the chlorine atom at the double bond. For the P=O group, and absorption band in the region 1250-1300 cm^{-1} is characteristic, this being observed in both of our samples.

The acid chloride of 2-chloro-5-phenoxypentene-1-phosphinic acid is a white, crystalline substance, exceedingly hygroscopic, readily soluble in benzene, less so in petroleum ether and almost insoluble in sulfuric ether. 2-Chloro-5-phenoxypentene-1-phosphinic acid is a silvery-white, crystalline substance, poorly soluble in water and readily soluble in alcohol. The esters of 2-chloro-5-phenoxypentene-1-phosphinic acid are viscous, yellowish liquids, soluble in organic solvents.

On reacting the calculated amount of alcoholic KOH solution with the dimethyl and diethyl esters of 2-chloro-5-phenoxypentene-1-phosphinic acid the corresponding esters of 5-phenoxypentyne-1-phosphinic acid are obtained

$$C_6H_5O(CH_2)_3CCl{=}CHPO(OR)_2 \xrightarrow[C_2H_5OH]{KOH} C_6H_5O(CH_2)_3C{\equiv}CPO(OR)_2$$

The substances obtained and their constants are shown in Table 2.

An attempt to obtain these esters by reacting the acid chloride of 2-chloro-5-phenoxypentene-1-phosphinic acid with alcohol and the calculated amount of triethylamine was unsuccessful. We obtained in this case the corresponding esters of 2-chloro-5-phenoxypentene-1-phosphinic acid.

*Measurement of IR - spectra was carried out by V. N. Smorchkov in the laboratory of I. V. Obreimov.

TABLE 1

Name	Formula	Yield, % theor.	B.p.(m.p.) °C (mm Hg)	n_D^{20}	d_4^{20}	MR calc.	MR found	Found, % C	Found, % H	Found, % P	Found, % Cl	Calculated, % C	Calculated, % H	Calculated, % P	Calculated, % Cl
Acid chloride of 2-chloro-5-phenoxypentene-1-phosphinic acid	$C_6H_5O(CH_2)_3CCl{=}CHPOCl_2$	32	64—66(пл.)	—	—	—	—	42,72 42,50	4,13 4,09	9,92 10,02	33,53	42,12	3,82	10,20	33,97
2-Chloro-5-phenoxypentene-1-phosphinic acid	$C_6H_5O(CH_2)_3CCl{=}CHPO(OH)_2$		108 (пл.)	—	—	—	—	47,87 47,73	4,99 5,03	11,29 11,26	13,14 13,08	47,73	5,06	11,21	12,83
Dimethyl ester of 2-chloro-5-phenoxypentene-1-phosphinic acid	$C_6H_5O(CH_2)_3CCl{=}CHPO(OCH_3)_2$	25	197—198(0,5)	1,5302	1,2333	75,57	76,28	51,33 51,57	6,16 6,06	10,07 9,98	11,74 11,83	51,20	5,91	10,11	11,65
Diethyl ester of 2-chloro-5-phenoxypentene-1-phosphinic acid	$C_6H_5O(CH_2)_3CCl{=}CHPO(OC_2H_5)_2$	28,5	199—200(2)	1,5135	1,1778	84,69	84,66	54,25 54,10	6,79 6,67	9,26 9,46	10,56 10,64	54,13	6,62	9,47	10,67
Dibutyl ester of 2-chloro-5-phenoxypentene-1-phosphinic acid	$C_6H_5O(CH_2)_3CCl{=}CHPO(OC_4H_9)_2$	32,2	220—221(1)	1,5023	1,1021	103,25	104,08	58,98 58,98	8,09 8,24	— —	— —	58,68	7,72	— —	—
Acid chloride of 2-chloro-5-ethoxypentene-1-phosphinic acid	$C_2H_5O(CH_2)_5CCl{=}CHPOCl_2$		139—142(3)	1,5112				31,57 31,70	4,27 4,37	—	—	31,64	4,52	—	—
Diethyl ester of 2-chloro-5-ethoxypentene-1-phosphinic acid	$C_2H_5O(CH_2)_5CCl{=}CHPO(OC_2H_5)_2$		158—160(3)	1,4680				46,29 46,15	7,69 7,65	—	—	46,39	7,73	—	—

TABLE 2

Name	Formula	Yield, % theor.	B.p., °C (mm Hg)	n_D^{20}	d_4^{20}	MR calc.	MR found	Found, % C	Found, % H	Calculated, % C	Calculated, % H
Dimethyl ester of 5-phenoxypentyne-1-phosphinic acid	$C_6H_5O(CH_2)_3C{\equiv}CPO(OCH_3)_2$	83	206(4)	1,5212	1,1504	69,08	70,47	58,40 58,56	6,69 6,65	58,20	6,34
Diethyl ester of 5-phenoxypentyne-1-phosphinic acid	$C_6H_5O(CH_2)_3C{\equiv}CPO(OC_2H_5)_2$	75	190(3)	1,5050	1,1091	78,31	78,15	61,14	7,30	60,81	7,09

EXPERIMENTAL

The 5-phenoxypentyne-1 used in the present work was prepared by reacting phenoxypropyl bromide with sodium acetylenide in liquid ammonia using the method of K. Campbell and B. Campbell [2]. The phenoxypropyl bromide was prepared using the method of Marvel and Tannenbaum [3] from 1,3-dibromopropane, which in turn was prepared using the method of Shostakovskii [4] and Antsus [5].

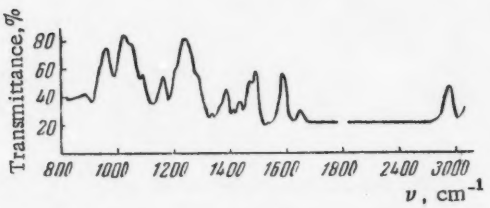

Fig. 1. IR - spectrum of the diethyl ester of 2-chloro-5-phenoxypentene-1-phosphinic acid.

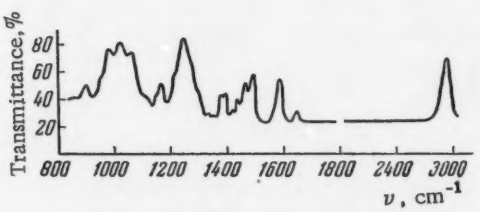

Fig. 2. IR-spectrum of the dibutyl ester of 2-chloro-5-phenoxypentene-1-phosphinic acid.

Acid chloride of 2-chloro-5-phenoxypentene-1-phosphinic acid. To a suspension of 83.4 g (0.4 M) of PCl_5 in absolute benzene was added dropwise 32 g (0.2 M) of 5-phenoxypentyne-1, diluted twice with absolute benzene. A bright-yellow precipitate of a complex then formed. On a subsequent day a stream of SO_2 was bubbled into the reaction mixture until the precipitate disappeared completely. After removal of solvent, $POCl_3$, and $SOCl_2$, the residue crystallized; m. p. 64-66° (after three recrystallizations from petroleum ether); yield 32% theoretical. The acid chloride of 2-chloro-5-ethoxypentene-1-phosphinic acid was synthesized similarly.

Dimethyl ester of 2-chloro-5-phenoxypentene-1-phosphinic acid. To 3 g of absolute methyl alcohol and 6.5 g of pyridine in absolute benzene was added dropwise with cooling with ice 12 g of the acid chloride of 2-chloro-5-phenoxypentene-1-phosphinic acid dissolved in an approximately equal volume of benzene. On the following day the reaction mixture was heated on a water bath for 2 hr, the precipitate of pyridine hydrochloride filtered off, the reaction mixture washed three times with 3% soda solution, then with water, and dried over Na_2SO_4. After removal of solvent, the residue was distilled in vacuo; yield 25.5% theoretical; b. p. 197-198° (0.5 mm); $n^{20}D$ 1.5302.

The diethyl and dibutyl esters of 2-chloro-5-phenoxypentene-1-phosphinic acid and the diethyl ester of 2-chloro-5-ethoxypentene-1-phosphinic acid were synthesized similarly.

Dimethyl ester of 5-phenoxypentyne-1-phosphinic acid. Four g of the dimethyl ester of 2-chloro-5-phenoxypentene-1-phosphinic acid was poured into a solution of 0.8 g of KOH in alcohol. The reaction mixture immediately evolved heat and a KCl precipitate settled out. The reaction mixture was heated on a water bath for 1 hr, the precipitate then filtered off, alcohol evaporated from the filtrate, and the residue distilled in vacuo. Three g of the dimethyl ester of 5-phenoxypentyne-1-phosphinic acid was obtained (75% theoretical); b. p. 206° (4 mm); $n^{20}D$ 1.5212. The diethyl ester of 5-phenoxypentyne-1-phosphinic acid was synthesized similarly.

2-Chloro-5-phenoxypentene-1-phosphinic acid. To 1 g of the acid chloride of 2-chloro-5-phenoxypentene-phosphinic acid was added a small amount of water. An oil then formed, which after several hours crystallized as silvery-white plates; m. p. 108° after recrystallizing twice from water.

SUMMARY

1. For the first time, the addition was accomplished of PCl_5 to 5-phenoxypentyne-1 and 5-ethoxypentyne-1.

2. 2-Chloro-5-phenoxypentene-1-phosphinic acid, its acid chloride and dimethyl, diethyl, and dibutyl esters were prepared and characterized, and also the acid chloride and diethyl ester of 2-chloro-5-ethoxypentene-1-phosphinic acid.

3. For the first time, the dimethyl and diethyl esters of 5-phenoxypentyne-1-phosphinic acid were prepared and characterized.

4. The IR -spectra were taken of the diethyl and dibutyl esters of 2-chloro-5-ethoxypentene-1-phosphinic acid.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ORGANOSILICON COMPOUNDS WITH HYDROCARBON BRIDGES BETWEEN SILICON ATOMS

COMMUNICATION 1. REACTION OF 1,2-DISILYLETHANES WITH METAL HALIDES

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Comparatively recently it became possible to synthesize various monomeric and polymeric compounds containing fragments of the type $\rangle Si-R-Si\langle$, where R is a hydrocarbon biradical. It is expected that materials obtained from polymeric compounds with the chains $-Si-R-Si-R-$ or $-Si-R-Si-O-$ will have a higher resistance toward aggressive media than silicon polymers [1] and, in some cases (arylene bridges) a high thermal stability and fiber-forming properties [2].

Nonetheless, the chemical properties of the grouping Si–R–Si have been studied quite inadequately. As a a subject for the present work we chose substances containing the disilylethane grouping $\rangle Si-CH_2-CH_2-Si\langle \equiv$ with methyl radicals and chlorine atoms at the silicon atoms. The action of metal halides with the properties of Lewis acids on these substances was investigated.

In accordance with the results of the reaction of 1,2-hexamethyldisilylethane with these metal halides, the latter could be divided into three groups:

Group I. Halides which do not react with hexamethyldisilylethane: $ZnCl_2$, $TiCl_4$, $SnCl_4$, BF_3 etherate, and $FeCl_2$ (in amounts of up to 40 mol. %).

Group II. $FeCl_3$ reacts to form only low-molecular compounds, namely, trimethylchlorosilane and, evidently, ethylene. This indicates simultaneous rupture of the Si–C bonds and elimination of the carbon chain (bridge). The decomposition evidently proceeds according to reaction schemes 1 and 2:

$$(CH_3)_3SiCH_2CH_2Si(CH_3)_3 + Fe_2Cl_6 \rightarrow (CH_3)_3SiCl + ClCH_2CH_2Si(CH_3)_2 + 2FeCl_2 \quad (1)$$

$$ClCH_2CH_2Si(CH_3)_3 \rightarrow CH_2=CH_2 + (CH_3)_3SiCl \quad (2)$$

Cases of the rupture of Si–C bonds in monosilanes have been reported in the literature [3].

Group III. Aluminum halides, which produced the formation of $Si(CH_3)_4$ and silicon-containing polymers. The temperature at which the reaction begins (Table 1) depends on the amount of catalyst taken. Moderate heating of $(CH_3)_3SiCH_2-CH_2Si(CH_3)_3$ with AlX_3 (10-40 mol. %) liberated 0.7-0.9 mole of $Si(CH_3)_4$ and then the reaction practically ceased. Simultaneously with the liberation of $Si(CH_3)_4$, in the reaction mixture there was formed a polymer, whose elementary analysis data corresponded to the polymer structural element $[-Si(CH_3)_2-CH_2-CH_2-]$. At first we were unable to isolate individual compounds from this polymer. We then carried out the reaction with the minimal amount of catalyst and stopped it when ~0.3 mole of $Si(CH_3)_4$ had been liberated. In this experiment we were able to isolate from the polymeric residue two individual compounds: $[-Si(CH_3)_2CH_2-CH_2-]_n$, where n = 2 and 3. A cyclic dimer of this type was obtained previously by Curry [4] by a reaction of a different type: $2(CH_3)HSiCH = CH_2 \xrightarrow{Pt/C} [-Si(CH_3)_2CH_2CH_2-]_2$. The properties of the preparations obtained by Curry and us were found to be

TABLE 1. Reaction of 1,2-Hexamethyldisilylethane* with Metal Halides

Metal halide	Amount, mol. % by wt..	Temp. of starting of reaction,** °C	Reaction products
$AlCl_3$	up to 5	Starting material recovered	
The same	10	120—125	$Si(CH_3)_4$/polymer
» »	40	<20	The same
$AlBr_3$	5	120—125	» »
The same	10	40—50	» »
$FeCl_3$	43	<20	$(CH_3)_3SiCl$***/$FeCl_2$

* A 30-60 g sample was usually used in a reaction.

** Temperature in the still over the range from the beginning of boiling of the mixture to the appearance of vapor of a low-boiling substance in the condenser.

*** An unsaturated gaseous product was liberated.

identical. The reaction products obtained and the capacity of aluminum halides to form reactive complexes with organosilicon compounds [5] made it possible to represent the reaction discovered by one of the general schemes (3) or (4).

$$(CH_3)_3SiCH_2CH_2Si(CH_3)_3 + Al_2X_6 \rightarrow (CH_3)_3SiCH_2CH_2Si(CH_3)_3 \cdot Al_2X_6$$

$$CH_3 \overset{|}{\underset{|}{\downarrow}} - Si(CH_3)_2CH_2CH_2 \overset{|}{\underset{|}{\downarrow}} Si(CH_3)_3 \cdot Al_2X_6 \rightarrow (SiCH_3)_4 + Al_2X_6 +$$

$$+ [-Si(CH_3)_2CH_2CH_2-]$$

$$_n[-Si(CH_3)_2CH_2CH_2-] \rightarrow [-Si(CH_3)_2CH_2CH_2-]_n \qquad (3)$$

$$(CH_3)_3SiCH_2CH_2 \overset{|}{\underset{|}{\downarrow}} Si(CH_3)_3 \cdot Al_2X_6 + CH_3 \overset{|}{\underset{|}{\downarrow}} Si(CH_3)_2CH_2CH_2Si(CH_3)_3 \rightarrow$$

$$\rightarrow (CH_3)_4Si + Al_2X_6 + (CH_3)_3SiCH_2CH_2Si(CH_3)_2CH_2CH_2Si(CH_3)_3 \qquad (4)$$

The linear dimer formed according to scheme [4] is converted analogously into linear polymers of the $(CH_3)_3SiCH_2CH_2[Si(CH_3)_2CH_2CH_2]_nSi(CH_3)_3$ or into cyclic polymers of the type $[-Si(CH_3)_2-CH_2-CH_2-]_n$; both processes proceed with the elimination of $(CH_3)_4Si$.

Thus, for example, the formation of a cyclic from a linear dimer is readily represented by scheme (5).

$$(CH_3) \overset{|}{\underset{|}{\downarrow}} Si(CH_3)_2CH_2CH_2Si(CH_3)_2CH_2CH_2 \overset{|}{\underset{|}{\downarrow}} Si(CH_3)_3 \xrightarrow{Al_2X_6} Si(CH_3)_4 +$$

$$+ (CH_3)_2Si\begin{matrix}CH_2CH_2\\ \diagup\quad\diagdown\\ CH_2CH_2\end{matrix}Si(CH_3)_2 \qquad (5)$$

We also studied the effect of substituents at the silicon in 1,2-disilylethanes on the direction of the polycondensation. It was established that the conversion of compounds with disilylethane groups occurs only when at least one of the silicon atoms is attached to three CH_3 radicals. The replacement of two or three methyl groups in $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ by chlorine led to a change in the composition of the low-boiling reaction products; di(methyldichlorosilyl)ethane and hexachlorodisilylethane did not react at all. The data in Tables 1 and 2 show that the disilylethanes investigated may be arranged in the following series with respect to their activity in the reaction with both $AlCl_3$ and $AlBr_3$: $(CH_3)_3SiCH_2CH_2Si(CH_3)_3 > (CH_3)_3SiCH_2CH_2Si(CH_3)Cl_2 > (CH_3)_3SiCH_2CH_2SiCl_3 \gg$ $\gg (CH_3)Cl_2SiCH_2CH_2SiCl_2(CH_3)$, $Cl_3SiCH_2CH_2SiCl_3$. In the case of disilylethanes containing one $Si(CH_3)_3$ group [with $Si(R)Cl_2$ as the other], judging by the low-boiling reaction products, the conversion proceeded according to reactions analogous to (3) and (4) and may be represented by schemes (6) and (7).

TABLE 2

Disilylethane*	Catalyst (C)	Mol. % of C	Temperature of beginning of reaction, °C	Low-boiling reaction products, mol. % on starting disilylethane
$Cl_3SiCH_2CH_2SiCl_3$	$AlCl_3$	up to 40		Starting material recovered
$Cl_2(CH_3)SiCH_2CH_2SiCl_2(CH_3)$	Same	up to 40		The same
$(CH_3)_3SiCH_2CH_2SiCl_3$	» »	40	130—150	$(CH_3)_3SiCl$(40,0); $(CH_3)_4Si$(10,0)*
$(CH_3)_3SiCH_2CH_2Si(CH_3)Cl_2$	» »	5	125—140	***
The same	» »	10	105—115	$(CH_3)_3SiCl$(65,0); $(CH_3)_4Si$(7,5)
» »	» »	40	***	$(CH_3)_3SiCl$(75,0); $(CH_3)_4Si$***;
$Cl_2(CH_3)SiCH_2CH_2Si(CH_3)Cl_2$	$AlBr_3$	up to 40		Starting material recovered
$Cl_3SiCH_2CH_2SiCl_3$	Same	Same		The same
$Cl_3SiCH_2CH_2Si(CH_3)_3$	»	5	160—170	***
The same	»	10	110—130	$(CH_3)_3SiCl$(29,0); $(CH_3)_4Si$(22,0)**
$Cl_2(CH_3)SiCH_2CH_2Si(CH_3)_3$	»	5	110—125	***
The same	»	10	75—110	$(CH_3)_3SiCl$(92,5), $(CH_3)_4Si$(5,0)

* A 35-70 g sample of the substance was used for a reaction.

** A small amount of a mixture of CH_3SiCl_3 and $(CH_3)_2SiCl_2$ (according to infrared analysis data) was isolated and its formation occured when the mixture was heated to 220°.

*** Not measured.

$$Cl_2(R)SiCH_2CH_2 \overset{|}{\underset{\downarrow}{}} Si(CH_3)_3 \cdot Al_2X_6 + Cl \overset{|}{\underset{\downarrow}{}} SiCl(R)CH_2CH_2Si(CH_3)_3 \rightarrow$$

$$\rightarrow (CH_3)_3SiCH_2CH_2SiCl(R)CH_2CH_2Si(R)Cl_2 + Al_2X_6 + (CH_3)_3SiCl \text{ etc.} \quad (6)$$

$$Cl_2(R)SiCH_2CH_2 \overset{|}{\underset{\downarrow}{}} Si(CH_3)_3 \cdot Al_2X_6 + CH_3 \overset{|}{\underset{\downarrow}{}} Si(CH_3)_2CH_2CH_2SiCl_2(R) \rightarrow$$

$$\rightarrow Si(CH_3)_4 + Al_2X_6 + Cl_2(R)SiCH_2CH_2Si(CH_3)_2CH_2CH_2Si(R)Cl_2$$

$$\text{etc., where } R = -Cl \text{ or } -CH_3 \quad (7)$$

The fact that $Si(CH_3)_4$ was formed in the reaction of AlX_3 with $(CH_3)_3SiCH_2CH_2SiCl_3$ indicates that the polycondensation observed proceeds at least partially according to scheme (4). Additional evidence in favor of scheme (4) was obtained in an experiment on the action of 10 mol. % of $AlBr_3$ on an equimolecular mixture of $(CH_3)_3SiCH_2-CH_2Si(CH_3)_3$ and $Cl_2(CH_3)SiCH_2-CH_2Si(CH_3)Cl_2$ (the tetrachloride alone did not change even when treated with 40 mol. % of $AlBr_3$). In this experiment the main product was $(CH_3)_3SiCl$, which could have been obtained here only by the intermolecular reaction (8).

$$(CH_3)_3SiCH_2CH_2 \overset{|}{\underset{\downarrow}{}} Si(CH_3)_3 \cdot Al_2Br_6 + Cl \overset{|}{\underset{\downarrow}{}} SiCl(CH_3)CH_2CH_2Si(CH_3)Cl_3 \rightarrow$$
$$\rightarrow (CH_3)_3SiCl + Al_2Br_6 + (CH_3)_3SiCH_2CH_2SiCl(CH_3)CH_2CH_2Si(CH_3)Cl_2 \quad (8)$$

A polycondensation of this type also occurs at least partially during the action of $AlCl_3$ on compounds containing a disilylethane group and a $-Si-O-Si-$ group. Thus, reaction (9) formed a considerable amount of a mixture of low-boiling methylsilyl chlorides in addition to the main product, namely, an α,ω-dichloride.

$$[ClSi(CH_3)_2CH_2CH_2Si(CH_3)_2]_2O + AlCl_3 \rightarrow$$
$$\rightarrow 2ClSi(CH_3)_2CH_2CH_2Si(CH_3)_2Cl + [AlOCl] \quad (9)$$

In the preparation of trialkylchlorosilanes from hexaalkyldisiloxanes and $AlCl_3$, no destruction products were detected [6].

TABLE 3. Properties of Starting Disilylethanes

Formula	B.p., °C	n_d^{20}	d_4^{20}	M.p., °C
$Cl_3SiCH_2CH_2SiCl_3$	201—202			26
$(CH_3)Cl_2SiCH_2CH_2SiCl_2(CH_3)$	209—211	—	—	32—33
$(CH_3)_3SiCH_2CH_2SiCl_3$*	180—182	1,4468	1,1005	—
$(CH_3)_3SiCH_2CH_2Si(CH_3)Cl_2$**	180—183	1,4433	0,9872	—
$(CH_3)_3SiCH_2CH_2Si(CH_3)_3$	150—152	0,7525	1,4200	—

* Found: Cl 44.2, 44.3%. $C_5H_{13}SiCl_3$. Calculated: Cl 44.7%. Found MR 57.2. Calculated MR 57.3.

** Found: Cl 33.0, 33.0%. $C_6H_{16}SiCl_2$. Calculated: Cl 33.0%. Found MR 57.8. Calculated MR 57.7.

The polycondensation we investigated, which is specific to organosilicon chemistry, also occurs in the case of other α,ω-hexamethyldisilylalkanes, $(CH_3)_3Si(CH_2)_nSi(CH_3)_3$; the compounds we investigated with n = 1, 3, 4, and 5 also reacted with aluminum halides to form $Si(CH_3)_4$ and a polymeric silicohydrocarbon, consisting of disilylalkane fragments.

EXPERIMENTAL

The disilylethane compounds were obtained by a known procedure [7] by the addition of vinylsilyl chlorides to silanes in the presence of H_2PtCl_6 and also methylation of the adducts obtained. The properties of the disilylethanes used in the reactions with metal halides are given in Table 3.

Reaction of $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ with $AlBr_3$. Into a flask with a descending condenser were placed 87 g (0.5 mole) of the disilylethane and 6.7 g (0.025 mole) of $AlBr_3$. The mixture was heated slowly and the evolution of $Si(CH_3)_4$ began at 120-125° (in the flask). Heating for 2.5 hr yielded 27 g of $Si(CH_3)_4$,* and then the mixture was cooled, decomposed with water with stirring, and extracted with ether. The ether extracts were dried with anhydrous $CaCl_2$. After removal of the ether, from the residue we isolated 30.0 g of the starting disilylethane and 4.9 g of a fraction with b.p. 165-169°. The residue, which consisted of a clear, viscous oil, corresponded to the empirical formula $SiC_4H_{10}[-Si(CH_3)_2CH_2CH_2]$ according to elementary analysis. Distillation of the residue (25.5 g) yielded 19 g of a condensate with b.p. 30(5) - 210° (2 mm) without signs of decomposition. The undistilled residue (4.9 g) was a viscous yellow oil, whose molecular weight (cryoscopically in benzene) was 530. Found: Si 32.39, 32.59; C 56.15, 56.07; H 11.30, 11.30%. SiC_4H_9. Calculated: Si 32.58; C 55.72; H 11.69%. [unit $-Si(CH_3)_2CH_2CH_2-$].

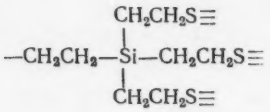
The condensate from vacuum distillation and the fraction with b.p. 165-169° (atm) were combined and distilled on a column to yield 5.5 g of $[-Si(CH_3)_2CH_2CH_2-]_2$ with b.p. 41-43° (8 mm) or 166-167° (atm) and d_4^{20} 0.8312; mol. wt. (cryoscopically in benzene) 170; calculated 172. Curry [4] reported for $[-Si(CH_3)_2CH_2CH_2-]_2$, b.p. 168-169°; n_D^{25} 1.4531; d_4^{25} 0.8277; mol. wt. 180 (found). We also isolated 3.5 g of $[-Si(CH_3)_2CH_2CH_2-]_3$ with b.p. 87-89° (3 mm); d_4^{20} 0.8463; n_D^{20} 1.4635; mol. wt. (cryoscopically in benzene) 252; calculated 258. Found: Si 32.95, 32.47; C 55.64, 55.42; H 11.52, 11.63%. $Si_3C_{12}H_{30}$. Calculated: Si 32.58; C 55.72; H 11.69%.

Investigation of the infrared spectra of the cyclic compounds isolated (analysis for $-CH_3$ and $-CH_2$ groups) confirmed their structure. An analogous reaction of $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ with 10-40% of AlX_3 formed a polymer, from which it was possible to isolate only 10-20% of a steadily boiling substance by distillation at 2 mm.** With the use of 10-40 mol. % of AlX_3, 0.7-0.95 mole of $(CH_3)_4Si$ per mole of disilylethane was usually liberated (with

* The only low-boiling reaction product: b.p. 26° (atm), d_4^{20} 0.6482; n_D^{20} 1.3595; the constants agree with literature data [8].

** Both the distillate and the undistilled residue obtained in these experiments corresponded to the formula $SiC_4H_{10}[-Si(CH_3)_2CH_2CH_2]$ according to elementary analysis data, while the infrared spectra of these substances contained intense bands with frequencies of 1130, 1055, and 1240 cm^{-1}, which Curry [4] reported as characteristic of polymers of the type $[-Si(CH_3)_2CH_2CH_2-]$.

moderate heating of the reaction mixture) and a clear, rubbery mass was formed, after which the liberation of $Si(CH_3)_4$ ceased. However, with further efficient heating, the liberation of $Si(CH_3)_4$ began again and thus the amount of tetramethylsilane reached 1.4-1.6 mole per mole of disilylethane, which is apparently explained by conversion of the linear polymer into a cross-linked one of the type:



Reaction of $(CH_3)_3SiCH_2CH_2Si(CH_3)Cl_2$ with $AlBr_3$. When 42 g (0.19 mole) of the dichloride was heated with 5.35 g (0.02 mole) of $AlBr_3$, the conversion of the dichloride began at 75-110°. After the liberation of 19 g of a condensate with b.p. 26-60°, the reaction ceased. Distillation of the condensate on a column in isooctane vapor yielded 0.8 g of $Si(CH_3)_4$ and 17.6 g of $(CH_3)_3SiCl$ with b.p. 57-58°; n_D^{20} 1.3855; d_4^{20} 0.8578. The residue was dissolved in benzene and treated with dry NaCl (to bind $AlBr_3$). After removal of the benzene, the residue consisted of a polymeric material containing hydrolyzable chlorine.

Reaction of a mixture of $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ and $Cl_2(CH_3)SiCH_2CH_2Si(CH_3)Cl_2$ with $AlBr_3$. A mixture of 16.2 g (0.093 mole) of hexamethyldisilylethane and 23.8 g (0.093 mole) of the tetrachloride was heated with 4.95 g (0.0186 mole) of $AlBr_3$. The polycondensation began at 100-110°. The condensate was fractionated analogously and consisted of 13.2 g (0.122 mole) of $(CH_3)_3SiCl$ and 4.6 g (0.052 mole) of $Si(CH_3)_4$, which correspond to 65 and 27 mol. %, respectively, on the total of disilylethanes taken.

Reaction of $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ with $FeCl_3$. For the reaction we used 15 g of $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ and 6 g (0.037 mole) of $FeCl_3$. The reaction began immediately when the reagents came in contact and a gas which decolorized bromine water was liberated. The condensate obtained by heating the mixture was distilled and found to consist of the starting disilylethane (8.3 g) with b.p. 148-150°; n_D^{20} 1.4200 and 3 g of $(CH_3)_3SiCl$, which corresponds to 75% of theoretical, calculated by equations (1) and (2). The residue from the reaction mixture was dissolved in water and extracted with ether. The ether extracts contained a further 2.1 g of the disilylethane, while the aqueous solution contained $FeCl_2$ (identified by reaction with potassium permanganate).

Synthesis of $[ClSi(CH_3)_2CH_2CH_2Si(CH_3)_2]_2O$. Vinyldimethylchlorosilane (b.p. 81-82°; n_D^{20} 1.4170; d_4^{20} 0.8915) was prepared from methylmagnesium chloride (30 g of Mg), which was added to 282 g of vinylmethyldichlorosilane; the yield was 46%. sym-Tetramethyldihydrodisiloxane was obtained by the procedure in [9].

Into a flask with a reflux condenser was placed $CH_2 = CHS(CH_3)_2Cl$ (15.8 g), the latter heated to boiling, one drop of a 0.1 N solution of H_2PtCl_6 in isopropanol added, and $H(CH_3)_2SiOSi(CH_3)_2H$ introduced in such a way that the temperature did not fall below 100°. The mixture was then boiled for a further 3 hr (up to 145°) and distilled. The $[ClSi(CH_3)_2CH_2CH_2Si(CH_3)]_2O$ was obtained in 67% yield and had b.p. 138-140° (7 mm); n_D^{20} 1.4508; d_4^{20} 0.9670; found MR 104.5; calculated MR 104.5. Found: Cl 18.9, 18.8%. $C_{12}H_{32}Si_4OCl_2$. Calculated: Cl 18.9%.

Reaction of $[Cl(CH_3)_2SiCH_2CH_2Si(CH_3)_2]_2O$ with $AlCl_3$. A mixture of 17.5 g of $[Cl(CH_3)_2SiCH_2CH_2Si(CH_3)_2]_2O$ and 6.3 g of $AlCl_3$ was heated in a Claisen flask. First there distilled a crystalline substance with b.p. 188-192° and then the temperature in the condensate vapor fell to 90-120° and a liquid distilled. Distillation of the condensate showed that it consisted of 1.9 g of a liquid with b.p. 25-70° (a mixture of methylsilyl chlorides according to spectral analysis data) and 14 g of 1,2-bis(dimethylchlorosilyl)ethane: m.p. 32-34°; found Cl 33.0, 33.2%; calculated Cl 33.0%. Infrared analysis of this substance confirmed that it contained a 1,2-disilylethane group.

The α,ω-dichlorodisilanes obtained could be used for the synthesis of polymers with alternating siloxane and disilylethane groups in the chain [10].

In conclusion, we would like to thank Yu. P. Egorov and L. A. Leitis who carried out the spectral analysis in the present work.

SUMMARY

1. The reaction of 1,2-hexamethyldisilylethane with a series of metal halides was studied. $FeCl_3$ is a reagent which cleaves the Si–C bond in the disilylethane grouping, while Al_2Br_6 and Al_2Cl_6 catalyze a polycondensation, which proceeds with the liberation of $Si(CH_3)_4$ and the formation of a polymer with disilylethane groups in the chain.

2. The reaction between Al_2X_6 and 1,2-disilylethanes containing various numbers of Si–Cl and Si–CH_3 groups was studied.

3. Two possible polymer-formation schemes are proposed for the polycondensation observed. Data were obtained supporting an intermolecular mechanism for the formation of a dimer (from $R_3SiCH_2CH_2SiR_3 \cdot Al_2X_6$ and $R'_3SiCH_2CH_2SiR'_3$ with the liberation of R_3SiR').

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STEREOCHEMISTRY OF HETEROCYCLIC COMPOUNDS

COMMUNICATION 2. GEOMETRIC ISOMERS OF 1-CYCLOHEXYL- AND 1-PHENYL-2,5-DIMETHYL-4-PHENYLPIPERIDOLS-4

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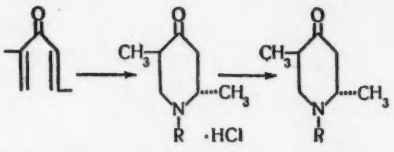
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 2, pp. 287-291, February, 1961
Original article submitted October 29, 1959

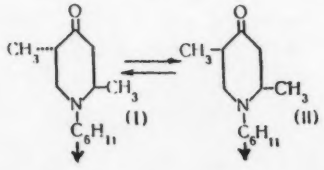
In previous work on the synthesis of 2,5-dimethylpiperidone-4 derivatives, it was shown that by condensation of propenyl isopropenyl ketone with cyclohexylamine and aniline it is possible to isolate pure hydrochlorides of 1-cyclohexyl and 1-phenyl-2,5-dimethyl piperidones-4, respectively [1, 2]. In view of the method by which they were prepared and isolated, these isomers apparently should have the methyl groups in the energetically more favorable trans-diequatorial position. The corresponding bases were obtained by careful liberation from the hydrochlorides and on treatment with phenyllithium each of them gave only one pure isomer of 1-cyclohexyl- and 1-phenyl-2,5-dimethyl-4-phenylpiperidol-4, respectively [3, 4]. In this stereoselective synthesis with phenyllithium, these N-substituted piperidones differ from 1,2,5-trimethylpiperidones-4 studied previously [5].

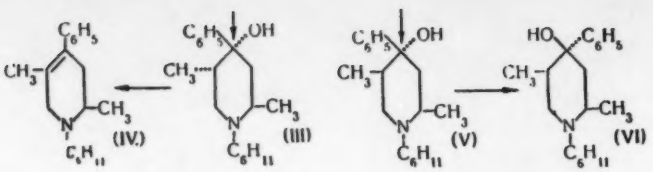


where R = C_6H_{11} or C_6H_5

A more detailed study of the pure crystalline 1-cyclohexyl-2,5-dimethylpiperidone-4 (m. p. 72-73°) made it possible to confirm its trans-configuration and to prepare the second isomer of this piperidone, which apparently had methyl groups in the cis-position. It was found that analogous to the conversion observed previously for 1,2,5-trimethylpiperidone, heating the crystalline trans-piperidone (I) with alumina at 100° formed an equilibrium mixture of the two geometric isomers (I) and (II), from which the starting trans-isomer separated on cooling. The remaining liquid isomerization product was the second isomer (II) in an almost pure state and in accordance with its configuration, by treatment with hydrogen chloride it was converted practically quantitatively into the hydrochloride of the more stable trans-isomer (I). Heating this cis-piperidone (II) with alumina again led to an equilibrium mixture of the two geometric isomers, from which crystalline 1-cyclohexyltrans-2,5-dimethylpiperidone-4 (I) was readily isolated on cooling.

As has already been mentioned above, the reaction of the crystalline trans-piperidone (I) with phenyllithium proceeded stereospecifically and gave only one geometrical isomer of 1-cyclohexyl-trans-2,5-dimethyl-4-phenylpiperidol-4 (III). In accordance with general conformational rules, the phenyl group in the product formed should occupy the more energetically favored equatorial posotion; as a result of this and with the axial hydroxyl, in this isomer there could have been favorable steric conditions for trans-diaxial elimination. In actual fact, the isomer (III) was found to undergo dehydration and treatment with thionyl chloride at room temperature with subsequent hydrolysis gave a good yield of an unsaturated product with m. p. 98-100° (apparently IV), whose structure, however, was not studied in more detail.

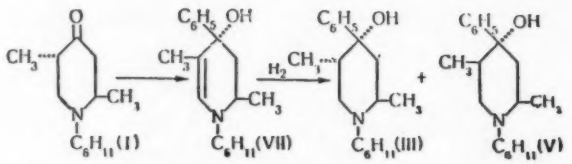




The reaction of phenyllithium with the isomeric cis-piperidone (II) also proceeded stereospecifically. In this case we obtained a good yield of only one isomer of 1-cyclohexyl-2,5-dimethyl-4-phenylpiperidol-4 (V), which at the same time confirmed that the starting liquid 1-cyclohexyl-cis-2,5-dimethylpiperidone-4 (II) was quite pure.

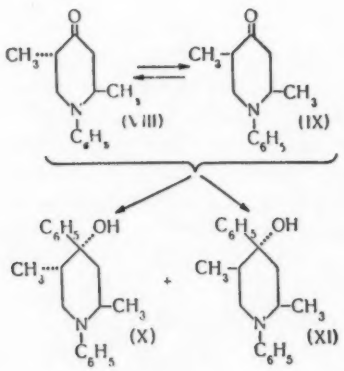
As was pointed out previously [5], in the case of isomeric phenylpiperidols with the methyl groups in the cis-position, the demonstration of the configuration may not be based solely on elimination or esterification reactions. However, certain experimental facts give us grounds for considering that the isomeric phenylpiperidol (V) obtained from the cis-piperidone (II) has the configuration with the phenyl and methyl groups in the cis-position. Thus, it was found that the phenylpiperidol (V) was dehydrated with comparative difficulty and treatment of the dehydration product with hydrogen bromide with subsequent hydrolysis gave a new isomeric 4-phenylpiperidol (VI), which differed from the other two. The cis-position of the methyl groups was apparently retained in the third isomer as it was shown previously that such elimination and hydration reactions lead predominantly to epimerization at C_4 as a result of the axial phenyl group moving into the energetically more favorable equatorial position.

If this is actually so, as a result of cis-addition of hydrogen, which could occur from both sides of the molecule, the catalytic hydrogenation of 1-cyclohexyl-2,5-dimethyl-4-phenyl-Δ^5-dehydropiperidol-4 (VII) should lead to a mixture of geometric isomers (III) and (V).



The procedure described previously [6] was used to prepare the unsaturated phenylpiperidol (VII) from 1-cyclohexyl-trans-2,5-dimethylpiperidone-4 (I), but unfortunately we were unable to isolate it in a pure state. Bromination of the trans-piperidone (I) with dehydrobromination and subsequent treatment with phenyllithium yielded an uncrystallizable mixture of products; however, after catalytic hydrogenation of this mixture it was possible to isolate small amounts of only the isomeric phenylpiperidones (III) and (V), which may serve as definite confirmation of the accuracy of the configurations proposed for them.

During a study of the stability of 1-phenyl-2,5-dimethylpiperidone-4, which was isolated previously [2], it was found that it also gave an equilibrium mixture of isomers when heated with alumina. However, in this case both possible isomeric trans- and cis-piperidones (VIII) and (IX) were found to be liquid and could not be isolated in pure states.



Its presence in the equilibrium mixture was demonstrated by the fact that treatment of the isomerization product with phenyllithium formed a mixture of the phenylpiperidone (X), which was described previously [4], and a second isomer of it (XI), which could be separated by crystallization. Since the isomer (X) is formed as the sole product by the reaction of phenyllithium with the trans-piperidone (VIII), which was isolated from its pure crystalline hydrochloride, it may be assumed that the second isomer (XI) was obtained from the cis-piperidone (IX). In accordance with this, the two isomeric 1,4-diphenyl-2,5-dimethylpiperidols-4 were assigned the configurations (X) and (XI) on the basis of the results described above for the corresponding N-cyclohexyl analogs.

EXPERIMENTAL

1-Cyclohexyl-cis-2,5-dimethylpiperidone-4 (II) and its conversions. A 55-g sample of 1-cyclohexyl-trans-2,5-dimethylpiperidone-4 (I) was stirred for half an hour with 1 g of alumina at 100°, the reaction mixture gradually cooled to 20°, the precipitated crystals collected, 0.5 g of Al_2O_3 added to them, the mixture stirred again for half an hour at 100° and cooled, and the unisomerized starting crystalline ketone collected. These operations were repeated four times to yield 42 g of a liquid mixture, which deposited 3 g of the starting trans-isomer on standing at 0° for a day. The remaining liquid isomerization product was vacuum distilled to yield 35 g of 1-cyclohexyl-cis-2,5-dimethylpiperidone-4 (II) with b. p. 118-120° (1 mm).

A solution of 1.9 g of the cis-isomer (II) in 20 ml of isooctane was saturated with dry hydrogen chloride. The precipitate oil was separated and treated with acetone. We obtained 1.5 g of 1-cyclohexyl-trans-2,5-dimethylpiperidone-4 hydrochloride with m. p. 172-173°, which has been described previously [1].

A mixture of 5 g of the cis-isomer (II) and 0.2 g of alumina was heated at 100° for 40 min and filtered. On cooling to 20°, the mixture deposited 1.7 g of the trans-isomer (I) with m. p. 72-73°, which was identical with that described previously.

1-Cyclohexyl-cis-2,5-dimethyl-4-phenylpiperidol-4 (V). A solution of 5 g of 1-cyclohexyl-cis-2,5-dimethylpiperidone-4 (II) in 5 ml of absolute ether was added with stirring over a period of 15 min to a solution of phenyllithium at 0° (from 1 g of lithium and 9 g of bromobenzene in 35 ml of ether). The reaction mixture was decomposed with 50 ml of water after 10 min and the precipitate collected. Recrystallization of this from isooctane yielded 4.3 g of 1-cyclohexyl-cis-2,5-dimethyl-4-phenylpiperidol-4 with m. p. 124-125°.

Found: C 79.05, 78.87; H 10.00, 10.10; N 4.86, 5.00%. $C_{19}H_{29}ON$. Calculated: C 79.40; H 10.10; N 4.88%. The hydrochloride had m. p. 239-240° (from alcohol). Found: N 4.13, 4.00%. $C_{19}H_{30}ONCl$. Calculated: N 4.31%.

Dehydration of 1-cyclohexyl-trans-2,5-dimethyl-4-phenylpiperidol-4 (III). To a suspension of 17 g of 1-cyclohexyl-trans-2,5-dimethyl-4-phenylpiperidol-4 (III), which was prepared previously [3], in 40 ml of chloroform was gradually added 40 ml of thionyl chloride. Vigorous evolution of gases occurred immediately and then the reaction mixture was boiled for one and a half hours and evaporated in vacuum. The residue was dissolved in the minimal amount of water and the solution filtered and boiled for 1 hr with 50 ml of a 25% aqueous solution of sodium hydroxide. The precipitate which formed when the solution was cooled was collected and recrystallized from heptane. We obtained 7.5 g of the dehydration product (IV) with m. p. 98-100°. Found: C 84.46, 84.48; H 10.08, 10.01%. $C_{19}H_{27}N$. Calculated: C 84.75; H 10.05%.

When the dehydration product (IV) was treated with hydrogen bromide in acetic acid with subsequent hydrolysis, a considerable part of its was recovered unchanged.

Isomerization of 1-cyclohexyl-cis-2,5-dimethyl-4-phenylpiperidol-4 (V). To a suspension of 22.5 g of the isomeric phenylpiperidol (V) in 50 ml of chloroform was gradually added 50 ml of thionyl chloride (no evolution of gases was observed) and then the mixture was boiled for one and a half hours and evaporated in vacuum. The residue was heated on a water bath for 1 hr with 100 ml of a 40% aqueous solution of sodium hydroxide; the hydrolysis product was extracted with ether and after removal of the ether, the crystalline reaction product was dissolved in acetic acid, treated with dry hydrogen bromide, and left overnight. After removal of the acetic acid in vacuum, the residue was shaken with 50 ml of water, heated at 100° for 2 hr, and then treated with excess ammonia. Recrystallization of the isomerization products from isooctane yielded ~2 g of a pure crystalline product, which, after a second recrystallization, had a constant m. p. 130-131° (from isooctane) and corresponded on analysis to the isomeric 4-phenylpiperidol (VI). Found: C 79.36, 79.30; H 10.06, 10.29%. $C_{19}H_{29}ON$. Calculated: C 79.40; H 10.10%.

Preparation of 1-cyclohexyl-cis- and trans-2,5-dimethyl-4-phenylpiperidols-4 through the unsaturated alcohol (VII). A 35-g sample of 1-cyclohexyl-2,5-dimethylpiperidone-4 hydrobromide was dissolved in 200 ml of hot water and 6.3 ml of bromine added to the warm solution. The thick yellow oil which precipitated dissolved after a few minutes, the solution became dark, and there formed a slight tarry precipitate, which was removed by filtration. The filtrate was cooled, saturated with sodium carbonate, and extracted with ether. After removal of the ether, 50 ml of triethylamine was added to the residue; the reaction mixture was boiled for 2 hr and then cooled and the triethylamine hydrobromide removed and washed with ether. Vacuum distillation yielded 2.5 g of the unsaturated piperidone (XII) with b.p. 130-150° (2 mm), which was treated with phenyllithium without further purification. A solution of 2.5 g of the unsaturated piperidone (XII) obtained above in 5 ml of ether was added to a solution of phenyllithium from 0.5 g of lithium and 4 ml of bromobenzene in 30 ml of ether. The reaction mixture was stirred at room temperature for 20 min, cooled to 0°, decomposed with 20 ml of water, and extracted with ether. The oil obtained after removal of the ether was hydrogenated in 20 ml of methanol over a mixture of Raney Ni and Pt, when 300 ml of hydrogen was absorbed in 6 hr. The catalyst was then removed by filtration, the filtrate evaporated, and the residue extracted with hydrochloric acid (1 : 1). The hydrochloric acid solution was washed with ether and treated with ammonia and the base liberated was extracted with heptane and vacuum distilled. We obtained 0.5 g of a fraction with b.p. 150-170° (2 mm), which was treated with heptane to yield 0.1 g of 1-cyclohexyl-cis-2,5-dimethyl-4-phenylpiperidol-4 (V) with m.p. 123-125°, that was identical with that described above. The mother heptane solution was treated with a saturated alcohol solution of hydrogen chloride to yield 0.1 g of the hydrochloride of 1-cyclohexyl-trans-2,5-dimethyl-4-phenylpiperidol-4 (III) with m.p. 257-258° (from acetone with ether), which was identical with that described previously [3].

Isomerization of 1-phenyl-trans-2,5-dimethylpiperidone-4 (II). 1-Phenyl-2,5-dimethylpiperidone-4 hydrochloride [4] was treated with a 50% solution of potassium hydroxide, the liberated oil extracted with isooctane, and the solution dried over solid potassium hydroxide and boiled for 1 hr with Al_2O_3 (3% of the weight of the piperidone). Vacuum distillation yielded an equilibrium mixture of the cis- and trans-isomers of 1-phenyl-2,5-dimethylpiperidones-4 (VIII) and (IX) with b. p. 120-125° (2 mm); $n^{18.5}D$ 1.5562.

Preparation of 1,4-diphenyl-cis- and trans-piperidones-4 (X) and (XI). A 3.5-g sample of the equilibrium mixture of piperidones (VIII) and (IX) obtained above was added to a solution of phenyllithium at 0° (from 1 g of lithium and 9 g of bromobenzene in 35 ml of ether). The reaction mixture was stirred at room temperature for 20 min and then decomposed with 50 ml of water. The ether layer was separated and evaporated to 15 ml and an equal volume of isooctane added to it. On standing, the solution gradually deposited 2.5 g of previously described 1-phenyl-trans-2,5-dimethyl-4-phenylpiperidol-4 (X) with m. p. 104-105° [4], which was identical with an authentic sample.

The ether-isooctane mother solution remaining after the separation of 1-phenyl-trans-2,5-dimethyl-4-phenylpiperidol-4 was saturated with dry hydrogen chloride and the precipitate recrystallized from alcohol. We obtained 0.3 g of the hydrochloride of 1-phenyl-cis-2,5-dimethyl-4-phenylpiperidol-4 (XI) with m. p. 237-239°. Found: C 72.16; H 7.67; N 4.72, 4.69%. $C_{19}H_{24}ONCl$. Calculated: C 71.49; H 7.56; N 4.48%.

After recrystallization from isooctane, the base isolated from this hydrochloride had m. p. 111-112° and sharply depressed the melting point of the isomer (X) described above. Found: C 81.00, 81.06; H 8.23, 8.22; N 5.64, 5.63%. $C_{19}H_{23}ON$. Calculated: C 81.04; H 8.53; N 4.98%.

SUMMARY

1- Isomerization of 1-cyclohexyl-trans-2,5-dimethylpiperidone with Al_2O_3 yielded 1-cyclohexyl-cis-2,5-dimethylpiperidone-4, which reacted with phenyllithium to give one isomer of 1-cyclohexyl-2,5-dimethyl-4-phenylpiperidol-4. On the basis of a series of chemical conversions, this isomer was assigned the configuration (V), which contains the methyl and phenyl groups in the cis-position.

2. Isomerization of the latter yielded a new isomer of this alcohol, which was apparently its epimer at C_4.

3. By analogous conversions of 1-phenyl-trans-2,5-dimethylpiperidone-4 it was possible to obtain the isomeric 1-phenyl-2,5-dimethyl-4-phenylpiperidol-4, which apparently had the methyl groups in the cis-position.

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SYNTHESIS OF FOUR GEOMETRICAL ISOMERS OF 1,2,3-TRIMETHYL-4-PHENYLPIPERIDOL-4

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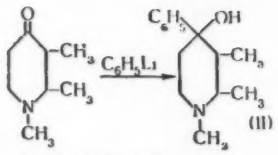
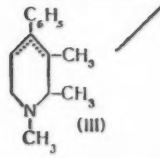
Original article submitted November 21, 1959

As was shown in a previous communication [1], 1,2,5-trimethylpiperidone-4 exists as an equilibrium mixture of cis- and trans-isomers, from which it was possible to obtain all four theoretically possible geometrical isomers of 1,2,5-trimethyl-4-phenylpiperidol-4 by treatment with phenyllithium. 1,2,3-Trimethylpiperidone-4 (I), which was described previously [2], should also be a mixture of the two possible isomers and in the present communication we describe the preparation of all the geometrical isomers of the corresponding phenyl alcohol from it.



α - m.p. 143–145°
β - m.p. 118–119°
γ - m.p. 96– 97°
δ - m.p. 109–111°

(I) cis and trans → (IIδ)



It was found that the reaction of phenyllithium with the piperidone (I) obtained after heating under alkaline conditions formed a mixture of the piperidols (II), from which we isolated in a total yield of 60% the pure isomers α, β, and γ in a ratio of 5.2: 3.8: 1. The fourth possible isomer (IIδ) was isolated by hydration of compound (III), which was obtained by dehydration of the α-isomer of the piperidol (II). By recrystallization of the hydrochloride obtained from the equilibrium mixture of piperidones, it was possible to obtain a pure hydrochloride and careful liberation of the base from this gave a pure isomer of the piperidone (I); its reaction with phenyllithium gave a mixture of only two isomers (β and γ) of the piperidol (II) in a ratio of 9: 1. Heating the pure piperidone (I) with alumina or alkali again led to a mixture of isomers, the reaction of which with phenyllithium formed the mixture of α-, β-, and γ-isomers described above. Thus, one isomer of the piperidone (I) gives two isomeric piperidols (IIβ and γ), while the other isomer of (I) gives mainly only one piperidol (IIα). These data indicate that the ratio of the cis- and trans-piperidones (I) in the equilibrium mixture is approximately 1: 1. Work is now being carried out to establish the configurations of the isomeric piperidones (I) and piperidols (II). The hydrochlorides of the propionic esters obtained from the piperidols (II) given above were tested fron analgesic activity and it was found that the β- and δ-isomers are inactive and the α-isomer has an activity equal to that of morphine, while the γ-isomer has an anesthetic activity more than 30 times as great as that of morphine.

EXPERIMENTAL

Synthesis of α-, β-, and γ-isomers of 1,2,3-trimethyl-4-phenylpiperidol-4 (II). A solution of 98.4 g (0.698 mole) of 1,2,3-trimethylpiperidone-4 [2] in 100 ml of ether was added over a period of 30 min with cooling in ice to the phenyllithium from 13.9 g (2.0 mole) of lithium and 157g of bromobenzene (1.0 mole) in 300 ml of ether; the reaction mixture was boiled for 30 min and treated with 460 ml of 5 N hydrochloric acid. The ether layer was discarded and the base extracted from the aqueous layer by treatment with 150 g of NaOH and extraction with ether.

The ether extracts were evaporated and the residue subjected to fractional crystallization from toluene and isooctane. We obtained 45 g of the α-isomer of 1,2,3-trimethyl-4-phenylpiperidol-4 with m. p. 143-145° (from toluene). Found: C 76.58; H 9.72; N 6.18%. $C_{14}H_{21}NO$. Calculated: C 76.70; H 9.58; N 6.37%; 33 g of the β-isomer of 1,2,3-trimethyl-4-phenylpiperidol-4 with m. p. 118-119° (from isooctane). Found: C 76.67; H 9.78; N 6.38%. $C_{14}H_{21}NO$. Calculated: C 76.70; H 9.58; N 6.37% and 9 g of the γ-isomer of 1,2,3-trimethyl-4-phenylpiperidol-4 with m. p. 96-97° (from isooctane). Found: C 76.61; H 9.73; N 6.30%. $C_{14}H_{21}NO$. Calculated: C 76.70; H 9.58; N 6.37%.

The α-isomer dissolved with difficulty in cold isooctane, toluene, and ether; its hydrochloride melted at 180-183° (from dichloroethane), and its picrate melted at 167-169° (from alcohol). The β-isomer was more soluble in ether, toluene, and isooctane than the α-isomer and its hydrochloride melted at 190-195° (from dichloroethane). The γ-isomer was isolated by concentrating the mother solutions after separation of the α- and β-isomers, converting the residues to the hydrochloride, and recrystallizing the latter from acetone and alcohol. The hydrochloride of the γ-isomer melted at 248°.

Treatment of 1,2,3-trimethylpiperidone-4 obtained from the hydrochloride with phenyllithium. A solution of 250 g of 1,2,3-trimethylpiperidone-4 [2] in an equal volume of isooctane was saturated with hydrogen chloride and the hydrochloride obtained in this way recrystallized from acetone. We obtained 230 g of 1,2,3-trimethylpiperidone hydrochloride with m. p. 151-152°. To 10 g of the hydrochloride obtained in this way was added liquid ammonia; the reaction mixture remaining after evaporation of the ammonia extracted with ether, and the ether extracts were vacuum distilled. We obtained 5 g of the base (I) with b. p. 70-71° at 9 mm and $n^{19.5}D$ 1.4661.

An ether solution of the piperidone obtained in this way was added to the phenyllithium from 0.7 g of lithium and 8.0 g of bromobenzene in 15 ml of ether at −30 to −40° over a period of 20 min. The reaction mixture was heated to room temperature and decomposed with 20 ml of water; the ether layer was separated and the residue, after evaporation of the ether, recrystallized from isooctane. We obtained 3.5 g of the β-isomer of 1,2,3-trimethyl-4-phenylpiperidol-4 with m. p. 118-120° and from the mother solutions we obtained a hydrochloride that was recrystallized to give 0.35 g of the hydrochloride of the γ-isomer of 1,2,3-trimethyl-4-phenylpiperidol-4, which did not depress the melting point of the hydrochloride obtained in the first experiment.

A 10-g sample of 1,2,3-trimethylpiperidone-4, liberated from the hydrochloride with alkali and distilled over Al_2O_3, was added to phenyllithium (from 1.4 g of lithium and 16 g of bromobenzene) in 30 ml of ether at −30 to −40° over a period of 30 min. The usual treatment yielded isomeric 1,2,3-trimethyl-4-phenylpiperdols in the same ratio as in the first experiment.

Synthesis of the δ-isomer of 1,2,3-trimethyl-4-phenylpiperidol-4. For synthesis by dehydration [3] of the α-isomer of 1,2,3-trimethyl-4-phenylpiperidol-4, a suspension of 125 g of the α-isomer of (II) in 200 ml of chloroform was saturated with hydrogen chloride and to the solution obtained in this way was added 250 ml of thionyl chloride. After the mixture had been boiled for 3 hr, the solvent and excess thionyl chloride were removed, the residue dissolved in water, and the solution saturated with NaOH. The base liberated was extracted with ether and vacuum distilled. The dehydration product distilled at 110-115° (2 mm) and the yield was 55 g.

For synthesis by hydration of 1-methyl-4-phenyl-1,2,5,6 (or 1,2,3,6)-tetrahydropyridine [4], the base obtained in the previous experiment was dissolved in 100 ml of CH_3COOH and the solution saturated with dry hydrogen bromide. On the following day the excess reagents were removed in vacuum and the residue dissolved in water and saturated with alkali. The base liberated was extracted with ether and vacuum distilled. We obtained 43 g of the starting compound with b. p. 110-115° (2 mm) and 11 g of a substance with b. p. 132-140° (2 mm). Recrystallization of the latter fraction yielded 9 g of the δ-isomer of 1,2,3-trimethyl-4-phenylpiperidol-4 with m. p. 109-111°. Found: N 6.87%. $C_{14}H_{21}NO$. Calculated: N 6.37%.

SUMMARY

All four theoretically possible geometrical isomers of 1,2,3-trimethyl-4-phenylpiperidol-4 were synthesized.

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SYNTHESIS AND PROPERTIES OF DI- AND TRIPHENYLALKANES

COMMUNICATION 4. SELECTIVE HYDROGENATION OF DI- AND TRIPHENYLALKANES OVER PtO_2

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In previous work [1-3] we prepared some mixed tricyclic hydrocarbons of the type $(C_6H_{11})_2(C_6H_5)CR$, where R = C_4, C_4-g , C_7, $-C-(C)_6$, $-C-(C)_4$, by selective hydrogenation of the corresponding triphenylalkylmethanes over Raney nickel, under a pressure of H_2, at temperatures of 100-140°. No hydrocarbons of the series $(C_6H_5)_2(C_6H_{11})CR$ or $(C_6H_{11})_3CR$ were formed under these conditions. The presence of two cyclohexyl rings at one carbon atom in the molecule apparently creates definite steric hindrance to the hydrogenation of the third ring. In the present investigation we continued the synthesis of di- and triphenyl alkanes, but mainly of a different type with the phenyl rings distributed along the chain, and platinum oxide was used as the hydrogenation catalyst. We prepared 1,7-diphenyl-4-(3-phenylpropyl)heptane, 1,1,1-tritolylheptane, and 1,7-diphenyl-4-(2-cyclohexylethyl)heptane by organomagnesium synthesis. The properties of all the hydrocarbons are given in the table.

The hydrogenation of the first two hydrocarbons over Raney nickel at 170-180° under a pressure of H_2 yielded 1,7-dicyclohexyl-4-(3-cyclohexylpropyl)-heptane and 1,1,1-trimethylcyclohexylheptane, which have not been described in the literature. Under the same conditions, 1,1,4,4-tetraphenylbutane and 1,1,6,6-tetraphenylhexane yielded 1,1,4,4-tetracyclohexylbutane and 1,1,6,6-tetracyclohexylhexane, respectively, which have not been described in the literature previously. The following hydrocarbons, some of which were synthesized for the first time and others previously, were hydrogenated over platinum oxide prepared by Adams' method [4]: 1,1,1-triphenylheptane, 1-phenyl-3-(2-phenylethyl)tridecane, 1,7-diphenyl-4-(2-phenylethyl)heptane, 1,5-diphenyl-3-(2-phenylethyl)pentane, 1,7-diphenyl-4-cyclohexylheptane, 1-phenyl-4-(3-phenylpropyl)decane, 1,1,4,4-tetraphenylbutane, and 1,1,6,6-tetraphenylhexane. It was found that 1,1,1-triphenylheptane, 1,1,1-tritolylheptane, 1,1,4,4-tetraphenylbutane, and 1,1,6,6-tetraphenylhexane do not add hydrogen at room temperature over platinum oxide. The other hydrocarbons added sufficient hydrogen for the hydrogenation of one ring and we obtained the following hydrocarbons with cyclohexyl and phenyl rings in the molecule which have not been described in the literature previously: 1,7-diphenyl-4-(3-cyclohexylpropyl)heptane, 1,5-diphenyl-3-(2-cyclohexylethyl)pentane, 1-phenyl-4,7-dicyclohexylheptane, 1-phenyl-4-(3-cyclohexylpropyl)decane, 1-cyclohexyl-4-(3-cyclohexylpropyl)decane, 1-phenyl-3-(2-cyclohexylethyl)tridecane, 1-phenyl-4-(2-phenylethyl)-7-cyclohexylheptane.

Most of these hydrocarbons were purified by chromatography on a two-stage column with a lower section 56.5 cm in height and 1.0 in diameter and an upper section 42.0 cm in height and 2.2 cm in diameter. The column was packed with 150 g of ASM grade silica gel. On comparing the properties of the hydrocarbons given in the table both with each other and with the properties of hydrocarbons prepared previously [1-3], one finds a series of new examples of changes in the properties of hydrocarbons as a result of changes in their structures. 1,1,1-Triphenylheptane, which was obtained previously, melted at 76.5°, while 1,1,1-tritolylheptane melted at 23°. 1,1,1-Triphenyldecane, which has the same molecular weight as the latter hydrocarbon, melted at 30°. The viscosity of 1,1,1-tritolylheptane was considerably greater than the viscosities of the other two hydrocarbons given. The product of complete hydrogenation of 1,1,1-tritolylheptane had a lower viscosity than the starting aromatic hydrocarbon. This is the first case of a fall in viscosity with a change from aromatic hydrocarbons to naphthenes among three-ring alkanes. The change to naphthenes is normally accompanied by a considerable increase in viscosity.

The 1,7-diphenyl-4-(3-phenylpropyl)heptane obtained in the present work melted at 5°, while a series of triphenylalkanes of similar structure, namely, 1,4,7-triphenylheptane, 1,7-diphenyl-4-benzylheptane, etc., [3] melted within the range of −25 to −35°. The viscosity of 1,7-diphenyl-4-(3-phenylpropyl)heptane was also greater than

Sample No.	Hydrocarbon	Formula	B.p. °C (p, mm Hg)	Solidification p., °C	d_4^{20}	n_D^{20}	MR found	MR calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H	Viscosity, centistokes 20°	50°	100°	150°
1	$(C_6H_5CH_2CH_2)_2CHCH_2CH_2C_6H_{11}$	$C_{25}H_{24}$	210—212(1)	—35, glass	0,9506	1,5300	108,63	108,25	89,30 89,25	10,80 10,70	89,74	10,26	107,75	21,55	9,6	2,12
2	$(C_6H_5CH_2CH_2CH_2)_3CH$	$C_{28}H_{34}$	260—262(5)	5, glass	1,0165	1,5710	119,7	120,7	90,70 90,72	9,13 9,23	90,74	9,26	—	173,74	13,47	3,98
3	$(C_6H_4CH_3)_3CC_6H_{13}$	$C_{28}H_{34}$	241—242(1)	23, glass	0,9932*	1,5710*	122,5	120,7	90,75 90,72	9,13 9,23	90,74	9,26	—	1454,6	30,15	5,45
4	$C_6H_5CH_2CH_2CH_2CHCH_2CH_2CH_2C_6H_{11}$ $\vert$ C_6H_{11}	$C_{25}H_{40}$	193—194(1)	—32, glass	0,9357	1,5140	109,52	109,30	87,27 87,23	11,78 11,78	88,15	11,85	170,14	25,37	4,03	1,61
5	$C_6H_5CH_2CH_2CH_2CHCH_2CH_2CH_2C_6H_{11}$ $\vert$ C_6H_{13}	$C_{25}H_{42}$	194—195(1)	—60, glass	0,8964	1,4970	111,77	111,85	87,90 87,73	12,11 12,11	87,61	12,39	68,46	10,47	2,58	1,21
6	$C_6H_5CH_2CH_2CH_2CHCH_2CH_2CH_2C_6H_{11}$ $\vert$ $CH_2CH_2C_6H_5$	$C_{27}H_{38}$	225—227(2)	—30, glass	0,9577	1,5318	117,23	117,49	89,24 89,33	10,52 10,80	89,40	10,60	65,0	20,53	4,65	2,05
7	$C_6H_5CH_2CH_2CH_2CH—CH_2CH_2CH_2C_6H_5$ $\vert$ $CH_2CH_2C_6H_{11}$	$C_{27}H_{36}$	185(0,5)	—23, glass	0,9685	1,5395	117,31	117,49	89,58 89,85	10,33 10,21	89,40	10,60	488,78	49,88	6,55	2,52
8	$C_6H_5CH_2CH_2CHCH_2CH_2C_6H_{11}$ $\vert$ $C_{10}H_{21}$	$C_{27}H_{46}$	207—208(1)	—50, glass	0,8885	1,4930	121,18	121,09	87,77 87,63	12,58 12,47	87,45	12,54	26,78	7,85	2,42	1,17
9	$(C_6H_{10}CH_3)_3C\cdot C_6H_{13}$**	$C_{28}H_{52}$	160—162(0,5)	—5, glass	0,9223	1,5080	125,57	124,90	87,35 87,59	12,30 12,10	86,50	13,50	3910,8	131,54	9,00	2,79
10	$(C_6H_{11}CH_2CH_2CH_2)_3CH$	$C_{28}H_{52}$	244(2)	0, glass	0,9251	1,5020	124,0	124,9	86,95 87,12	13,18 13,19	86,49	13,51	8750,0	945,38	20,91	5,35
11	$(C_6H_5CH_2CH_2CH_2)_2CHCH_2CH_2CH_2C_6H_{11}$	$C_{28}H_{40}$	213—215(0,5)	—10, glass	0,9651	1,5380	122,37	122,10	88,49 88,67	11,38 11,56	89,27	10,73	2660,6	167,47	13,60	4,03
12	$C_6H_{11}CH_2CH_2CH_2CHCH_2CH_2CH_2C_6H_{11}$ $\vert$ C_6H_{13}	$C_{25}H_{48}$	192(1)	—55, glass	0,8682	1,4760	113,24	113,25	86,10 86,13	13,83 13,91	86,01	13,92	46,31	11,68	5,22	2,07
13	$(C_6H_{11})_2CHCH_2CH_2CH(C_6H_{11})_2$	$C_{28}H_{50}$	—	—80, crystals	—	—	—	—	86,93 86,97	13,03 12,95	86,93	13,07	—	—	—	—
14	$(C_6H_{11})_2CHCH_2CH_2CH_2CH_2CH(C_6H_{11})_2$	$C_{30}H_{54}$	—	—127, crystals	—	—	—	—	86,80 86,79	12,94 12,90	86,85	13,15	—	—	—	—

*At 40°.

**Mol. wt. 386.5; calculated 388.

the viscosities of the other hydrocarbons given. On the basis of the latter circumstance we first assumed that the dehydration of the corresponding alcohol, namely, 1,7-diphenyl-4-(3-phenylpropyl)heptanol-4 resulted in the formation of a hydrindan ring in the molecule, the more so as this alcohol required considerably more drastic conditions for dehydration than alcohols of similar structure. However, the ultraviolet spectrum of the hydrocarbon indicated that the molecule contained only benzene rings. The increase in viscosity and the rise in solidification point are apparently explained solely by the higher symmetry of the molecule $(C_6H_5-CH_2CH_2CH_2)_3CH$. The small rule holds for the products of complete hydrogenation of the hydrocarbons given. An increase in the side chain from C_6H_{11} to $CH_2CH_2C_6H_{11}$ lowered the solidification point from −20 to −25° and the viscosity from 423 to 279 centistokes at 20° and from 49 to 35 centistokes at 50°. A further increase in the side chain to $CH_2CH_2CH_2C_6H_{11}$ raised the solidification point to 0° and the viscosity to 8750 centistokes at 20° and 945 centistokes at 50° and this can also be explained by the higher symmetry of the molecule $(C_6H_{11}CH_2CH_2CH_2)_3CH$.

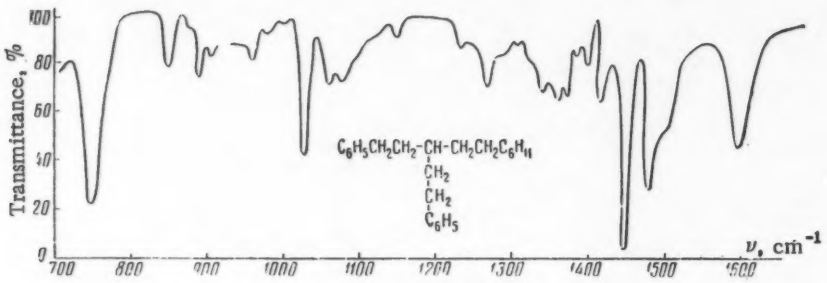

Fig. 1.

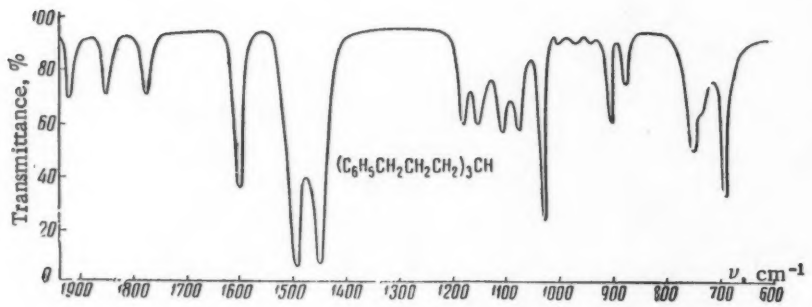

Fig. 2.

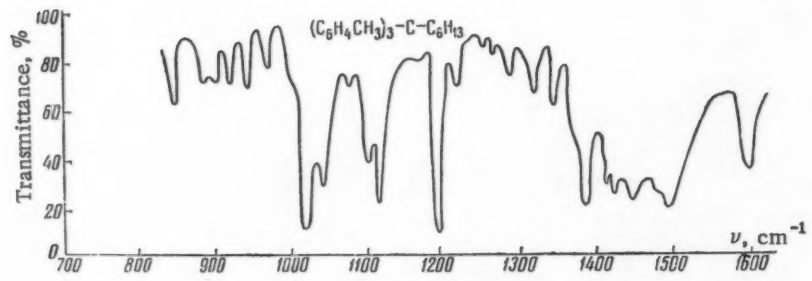

Fig. 3.

With the naphthene–aromatic hydrocarbons we obtained, the solidification point was often lower and the viscosity higher than in the case of the starting aromatic hydrocarbons. The viscosities of the complete hydrogena-

tion products were even higher. Thus, for example, 1,5-diphenyl-3-(2-phenylethyl)pentane solidified at −32° [5] and the corresponding naphthene melted at 41° [5], while 1,5-diphenyl-3-(2-cyclohexylethyl)pentane solidified at −35°. In exactly the same way, 1-phenyl-4,7-dicyclohexylheptane solidified at a lower temperature than 1,4,7-triphenyl- and 1,4,7-tricyclohexylheptanes [3].

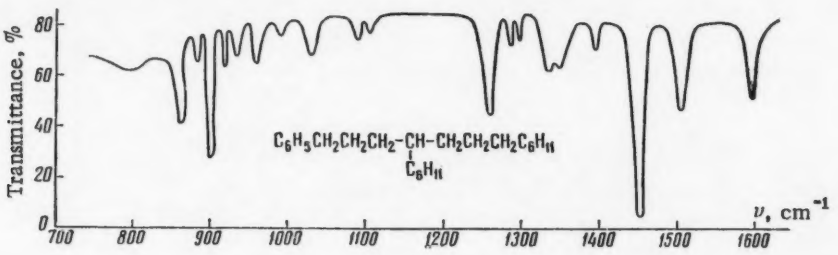

Fig. 4.

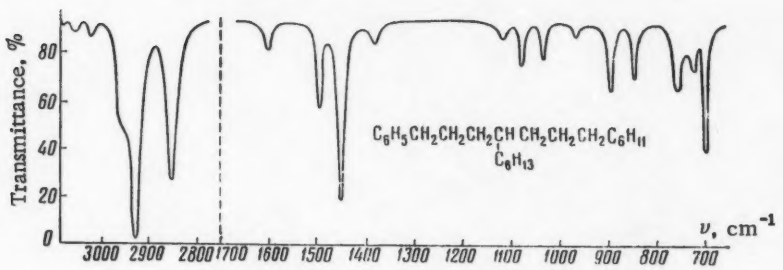

Fig. 5.

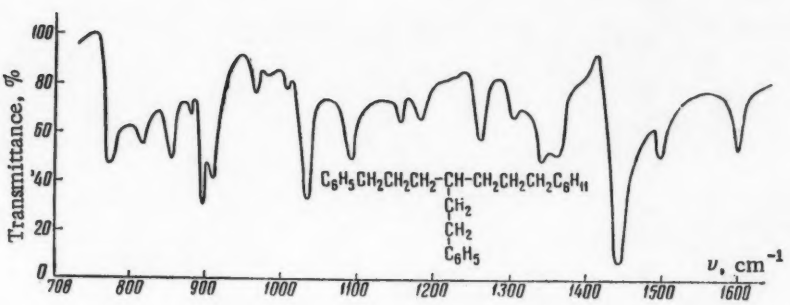

Fig. 6.

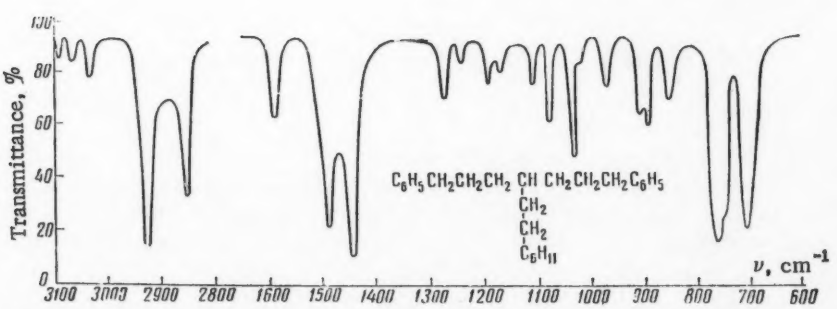

Fig. 7.

We consider that in the hydrogenation of 1,7-diphenyl-(2-phenylethyl)heptane, the ring farthest from the center of the molecule was hydrogenated. This was confirmed to some extent by the difference in the properties of this hydrocarbon and those of 1,7-diphenyl-4-(2-cyclohexylethyl)heptane, which we synthesized (Table No. 6 and 7).

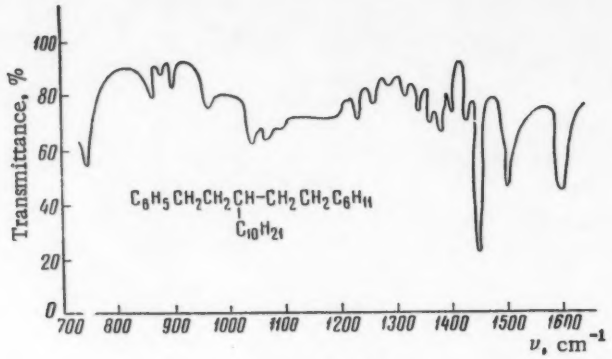

Fig. 8.

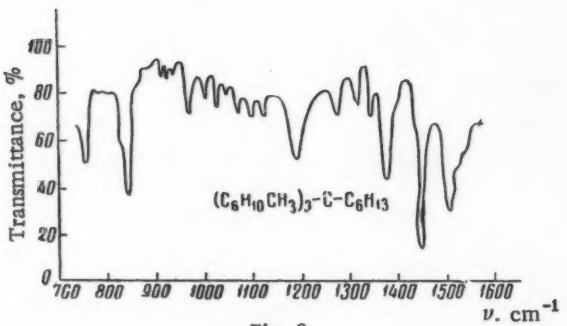

Fig. 9.

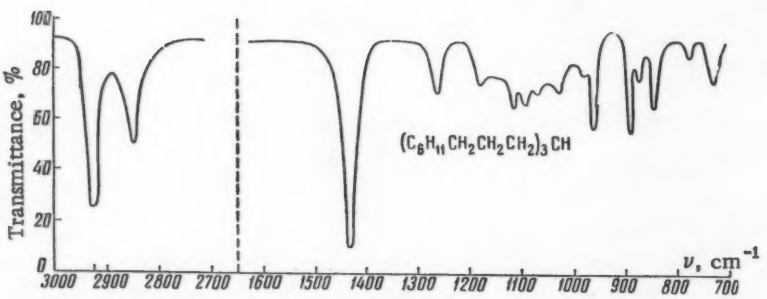

Fig. 10.

We plotted the infrared spectra of all the hydrocarbons we obtained and the ultraviolet spectrum of $(C_6H_5CH_2CH_2CH_2)_3CH$. The infrafred spectra of $(C_6H_4CH_3)_3C-C_6H_{13}$ and $(C_6H_{10}CH_3)_3C-C_6H_{13}$ contained bands with frequencies of 850, 1070, 1080, 1500, 1600, and 1110 cm^{-1} in the first case and 906 and 1250 cm^{-1} in the second case, which correspond to disubstituted aromatic and naphthene hydrocarbons. The spectral data are given as curves in Figs. 1-12.

EXPERIMENTAL*

1,7-Diphenyl-4-(3-phenylpropyl)heptane. From $C_6H_5CH_2CH_2CH_2MgBr$ (320 g of phenylpropyl bromide) and 118 g of ethyl phenylbutyrate we obtained 168 g (71% yield) of 1,7-diphenyl-4-(3-phenylpropyl)heptanol-4 with b. p. 233° (1 mm); d^{20}_4 1.0137; $n^{20}D$ 1.5660; MR found 123.68; MR calculated MR 123.26. Found: C 87.70; H 9.14; OH 4.83%. $C_{28}H_{34}O$. Calculated: C 86.98; H 8.88; OH 4.40%.

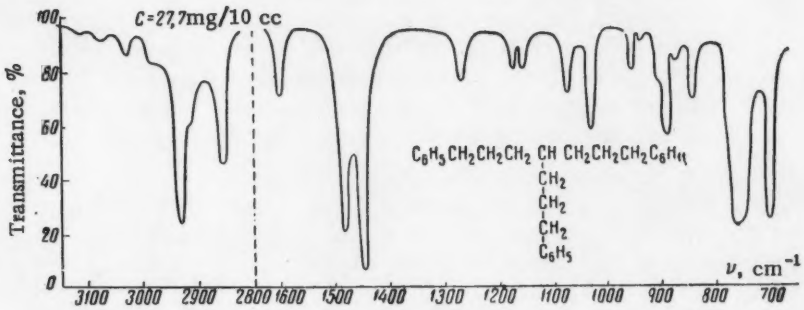

Fig. 11.

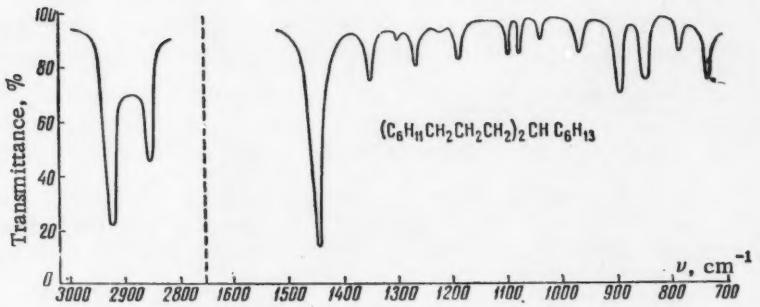

Fig. 12.

The alcohol obtained was dehydrated by the method in [6] to yield 78 g (49%) of 1,7-diphenyl-4-(3-phenylpropyl)heptene-4 with b. p. 234° (1 mm), solidification p. −6°; d^{20}_4 1.0208; $n^{20}D$ 1.5750; MR found 119.23; MR calculated 120.23. Found: C 90.96; H 9.00%. Calculated: C 91.23; H 8.77%. Viscosity in centistokes: ν^{20} 1067.2; ν^{50}77.24; ν^{100} 9.30; ν^{150} 3.12.

The unsaturated hydrocarbon was hydrogenated under a pressure of H_2 in an autoclave at 40-50° with Raney nickel. We obtained 68 g of 1,7-diphenyl-4-(3-phenylpropyl)heptane. A 26-g sample of the latter was hydrogenated over 0.22 g of PtO_2 in 76 ml of acetic acid. The amount of hydrogen added was 4.1 liters (theoretical 4.7 liters). Chromatography twice yielded 5 g of $(C_6H_5CH_2CH_2CH_2)_2CHCH_2CH_2CH_2C_6H_{11}$.

1,1,1-Tritolylheptane. From $MgBrC_6H_{13}$ (83 g, 0.5 mole of hexyl bromide) and 75 g (0.23 mole) of $(C_6H_4CH_3)_3CCl$ we obtained 26 g of the hydrocarbon, whose properties are given in the table. An 11-g sample of 1,1,1-tritolylheptane was hydrogenated under a pressure of H_2 in an autoclave at 180-200° over Raney nickel (3 g) for 20 hr. We obtained 6 g of 1,1,1-trimethylcyclohexylheptane.

1,7-Diphenyl-4-(2-cyclohexylethyl)heptane. From $C_6H_5CH_2CH_2CH_2MgBr$ (42 g of $C_6H_5CH_2CH_2CH_2Br$) and 18.5 g of ethyl cyclohexylpropionate we obtained 17 g of a product with b. p. 200-235° (1 mm), which was a mixture of 1,7-diphenyl-4-(2-cyclohexylethyl)-heptanol-4 and the corresponding olefins and 3 g of pure alcohol with b. p. 245° (1 mm); d^{20}_4 0.9988; $n^{20}D$ 1.5410; MR found 119.05; MR calculated 119.01. Found: C 85.42; H 10.27; OH 5.85%. $C_{27}H_{38}O$. Calculated: C 85.62; H 10.15; OH 4.54%.

*Laboratory assistant V. P. Krukhtanova helped with the experimental work.

Without preliminary separation, the mixture of alcohol and olefin was dehydrated by the method in [6]. The olefins obtained had b. p. 212-220° (1 mm); d^{20}_4 0.9826; $n^{20}D$ 1.5490; MR found 116.67; MR calculated 117.01. A 10.5 g sample of the mixture of olefins was hydrogenated in 20 ml of acetic acid over 0.08 g of PtO_2 at ~20°. The amount of hydrogen required for the hydrogenation of one double bond (620 ml) was added. The hydrocarbon, which had a bromine number of zero, was chromatographed.

1,5-Diphenyl-3-(2-cyclohexylethyl)pentane. From $C_6H_5CH_2CH_2MgBr$ (185 g of $C_6H_5CH_2CH_2Br$) and 89 g of ethyl hydrocinnamate we obtained 124 g of 1,5-diphenyl-3-(2-phenylethyl)pentanol-3; the latter was dehydrated by the method in [6] to yield 100 g of 1,5-diphenyl-3-(2-phenylethyl)pentene-3 with b. p. 205° (2 mm); $n^{20}D$ 1.5860. Literature data [5]: b. p. 210.5° (1 mm); d^{20}_4 1.0159; $n^{20}D$ 1.5816. A 29 g sample of the latter was hydrogenated in 70 ml of acetic acid over 0.23 g of PtO_2. The amount of hydrogen absorbed was 6.2 liters. The amount of hydrogen required for the hydrogenation of one phenyl ring and one double bond was 8.3 liters. Chromatography twice yielded 14 g of 1,5-diphenyl-3-(2-phenylethyl)pentane and 10 g of 1,5-diphenyl-3-(2-cyclohexylethyl)pentane.

1-Phenyl-4,7-dicyclohexylheptane. A 12-g sample of 1,7-diphenyl-4-cyclohexylheptene-4 was hydrogenated over 0.1 g of PtO_2 in 30 ml of acetic acid. The amount of hydrogen absorbed was 2.73 liters, while the amount of hydrogen required for the hydrogenation of one double bond and one ring was 3.17 liters. We obtained 8.3 g of a product. The experiment was repeated with 8 g of 1,7-diphenyl-4-cyclohexylheptane, 0.0949 g of PtO_2, and 23 ml of acetic acid. We obtained 5.5 g of product. The two incomplete hydrogenation products were mixed and chromatographed twice. We obtained 6.4 g of 1-phenyl-4,7-dicyclohexylheptane.

1-Phenyl-4-(3-cyclohexylpropyl)decane. A 20 g sample of 1-phenyl-4-(3-phenylpropyl)decane was hydrogenated in 50 ml of acetic acid over 0.18 g of PtO_2 at 20°. The amount of hydrogen required for the hydrogenation of one ring was 4.0 liters and 4.5 liters of hydrogen was actually absorbed. Chromatography twice yielded 8 g of 1-phenyl-4-(3-cyclohexylpropyl)decane and 4.7 g of 1-cyclohexyl-4-(3-cyclohexylpropyl)decane.

1-Phenyl-3-(2-cyclohexylethyl)tridecane. A 4-g sample of 1-phenyl-3-(2-phenylethyl)tridecane was hydrogenated in 10 ml of acetic acid over 0.03 g of PtO_2 at ~20°. The amount of hydrogen required for the hydrogenation of one ring was 0.73 liter and 0.71 liter of hydrogen was absorbed. We obtained 2.9 g of the hydrocarbon.

1-Phenyl-4-(2-phenylethyl)-7-cyclohexylheptane. An 8.5-g sample of 1,7-diphenyl-4-(2-phenylethyl)heptane was hydrogenated over 0.12 g of PtO_2 in 40 ml of acetic acid. The amount of hydrogen required for the hydrogenation of one ring was 0.73 liter and 0.71 liter was absorbed. Chromatography twice yielded 5.6 g of the hydrocarbon.

In conclusion, the authors would like to thank Yu. P. Egorov and E. Lubush for plotting the spectra.

SUMMARY

1. 1,7-Diphenyl-4-(3-phenylpropyl)heptane, 1,7-dicyclohexyl-4-(3-cyclohexylpropyl)heptane, 1,1,1-tritolylheptane, 1,1,1-tricyclohexylheptane, and 1,7-diphenyl-4-(2-cyclohexylethyl)heptane were prepared for the first time by organomagnesium synthesis.

2. The following hydrocarbons were obtained by selective hydrogenation of the corresponding triphenylalkanes over PtO_2: 1,7-diphenyl-4-(3-cyclohexylpropyl)heptane, 1,5-diphenyl-3-(2-cyclohexylethyl)pentane, 1-phenyl-4,7-dicyclohexylheptane, 1-phenyl-4-(2-cyclohexylpropyl)decane, 1-cyclohexyl-4-(3-cyclohexylpropyl)decane, 1-phenyl-3-(2-cyclohexylethyl)tridecane, and 1-phenyl-4-(2-phenylethyl)-7-cyclohexylheptane.

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CHEMICAL COMPOSITION OF CRACKED GASOLINES FROM NAPHTHENIC CRUDE

COMMUNICATION 2. INVESTIGATION OF INDIVIDUAL HYDROCARBON COMPOSITION OF CRACKED GASOLINES FROM SURAKHAN SELECT CRUDE

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In a previous communication [1] we set forth in detail the separation of fractions from three thermally and catalytically cracked gasolines (gasolines 2, 11, and 12, produced from distillates of Surakhan select crude), boiling up to 60°, 60-95°, 95-122°, 122-150°, and 150-175°; this communication also covered the chromatographic separation of the 60-175° fractions into naphthenic-paraffinic, unsaturated, and aromatic hydrocarbons and the method of investigating the detailed group hydrocarbon composition of the 60-175° fractions of these same gasolines. The subject of the present communication is the study of the hydrocarbon composition of the fractions of gasolines 12, 2, and 11 taken up to 60°, and the investigation of the aromatic hydrocarbons present in the 60-175° fractions of those same gasolines.

EXPERIMENTAL

Investigation of composition of fractions taken up to 60°. Of the above-enumerated fractions, the fraction taken up to 60° was separated into narrow fractions by refractionation in a column with 45 theoretical plates. The characteristics of the fractions recovered are shown in Table 1. As is evident from Table 1, the light fractions of the gasolines differ markedly among themselves in physicochemical characteristics. The individual hydrocarbon composition of the fractions taken up to 26.5° was investigated in a gas–liquid chromatography unit [2]. The composition of the fractions taken within the 26.5-60° range was analyzed by a spectral method based on combination dispersion [Raman] spectra according to a method described previously [3]. The total data on the hydrocarbon composition of the head fractions of the three gasolines, taken up to 60°, are compared in Table 2.

From a comparison of the data obtained it is evident that the ratio of the content of total normal and branched paraffins in the IBP-60° fractions of gasoline 2 to the content of the corresponding hydrocarbons in the IBP-60° fraction of gasoline 11 is equal to 1.4:1, and the ratio for total olefins and cycloolefins is 0.77:1. The ratios of normal paraffins to isoparaffins for the IBP-60° fractions of gasolines 2 and 11 are close to each other and are equal to 1.4:1. For those same fractions of the gasolines the ratio of concentrations of normal olefins to the concentrations of isoolefins is not more than 0.5:1. Qualitative analysis indicates the presence in each of the gasolines investigated (IBP-60° fraction) of approximately 30 individual hydrocarbons. Quantitative analysis reveals profound differences in the concentrations of the individual components found in the IBP-60° fractions of the gasolines.

In the IBP-60° fraction of the catalytically cracked gasoline (G-12) there are only four hydrocarbons present in concentration exceeding 5%: 2-methylbutane (36.4%), 2-methylbutene-2 (15.1%), 2-methylpentane (8.6%), and n-butenes (total of 1- and 2-isomers 6.5%). In these four hydrocarbons there is 66.6% of the total IBP-60° fraction. In the fractions of each of the thermally cracked gasolines (G-2 and G-11) there are eight hydrocarbons present in concentrations exceeding 5%, and six hydrocarbons exceeding 7%. In G-2, in order of decreasing concentrations: n-pentane (25.0%), 2-methylbutane (11.1%), 2-methylbutene-2 (> 7.9%), 2-methylpentane and 4-methylpentene-1 (7.5% each), pentene-1 (7.2%), total > 66.2%. In G-11: n-pentane (19.9%), 4-methylpentene-1 (12.0%), 2-methylbutene-2 (10.0%), pentene-1 (7.7%), 2-methylbutane (7.4%), cyclopentane (7.2%), total 64.2%. If it is considered

TABLE 1. Yield and Characteristics of Narrow Fractions of Gasolines 12, 2, and 11 Taken up to 60°

Fraction	Cut points, °C	Gasoline 12 (from catalytic cracking of kerosene–gas oil fraction)					Gasoline 2 (from thermal cracking of mazut [residual stock])					Gasoline 11 (from thermal cracking of kerosene–gas oil fraction)				
		yield on IBP-60° gasoline, wt. %	yield on IBP-150° gasoline, wt. %	n_D^{20}	d_4^{20}	iodine number	yield on IBP-60° gasoline, wt. %	yield on IBP-150° gasoline, wt. %	n_D^{20}	d_4^{20}	iodine number	yield on IBP-60° gasoline, wt. %	yield on IBP-150° gasoline, wt. %	n_D^{20}	d_4^{20}	iodine number
I	to 26,5	39,7	10,7	—	—	—	24,7	2,7	1,3581	—	176	20,2	1,9	1,3625	—	221,6
II	26,5—32	20,3	5,4	1,3585	0,6254	80	13,5	1,5	1,3660	0,6350	212	10,5	1,0	1,3670	0,6435	284
III	32—38	19,9	5,4	1,3825	0,6554	324	34,9	3,8	1,3698	0,6404	169,7	33,8	3,1	1,3720	0,6447	196,4
IV	39—46	1,8	0,5	1,4111	0,7390	325	2,7	0,3	1,4026	0,7156	242,4	6,5	0,6	1,4150	0,7511	298
V	46—56	2,7	0,7	1,3903	0,6723	202,5	12,7	1,4	1,3870	0,6813	221,4	21,1	1,9	1,3891	0,6849	224,5
VI	56—60	15,6	4,3	1,3753	0,6590	46,2	11,5	1,2	1,3770	0,6614	97,0	7,9	0,7	1,3780	0,6627	105,0
I—VI	IBP - 60	100	27,0				100	10,9				100,0	9,2			

that G-11 and G-12 were produced from the same feedstock and that the yield of the IBP-60° fraction in G-12 is considerably higher (27%, against 9.2% in G-11), the differences in the nature of the gasolines (connected with the method of their processing) stand out with extra clarity. In G-12 the concentration of 2-methylbutane is five times greater than in G-11, n-butenes two times, 2-methylpentane 1.6, times, and 2-methylbutene-2,1.5 times greater; but the concentration of n-pentane in G-12 is 50 times less than in G-11, n-pentene-1, 15 times, 2-methylbutene-1 more than five times, and n-trans-pentene-2,1.5 times less.

The differences of the light fractions of G-2 and G-11, which are obtained with yields of 11 and 9.2% respectively from heavy and light raw material by an identical processing method, are shown less markedly, although clearly enough. In G-2 the concentration of n-butane is 2.4 times greater than in G-11, n-butenes 1.5 times, 2-methylbutane 1.4 times, and n-pentane 1.3 times greater; but the concentrations of n-trans-pentene-1, 4-methylpentene-1, and cyclopentane in G-2 are reduced almost twofold in comparison with G-11, and the concentration of cyclopentene is probably four times less.

The head fractions of the catalytically cracked gasoline apparently can be appraised as potential raw material for petrochemical synthesis on the basis of isopentane, 2-methylbutene-2, and 2-methylpentane. This is favored by their high relative concentration, which alleviates the problem of recovery from a mixture with a great number of other components. From the head fractions of the thermally cracked gasolines it is relatively easier to obtain n-butane, n-pentane, and such α-olefins as n-pentene-1, 2-methylbutene-1, and 4-methylpentene-1.

Investigation of composition of aromatic fractions 60-175°. The narrow fractions of the gasolines which were taken within the limits of 60-175° were separated chromatographically on silica gel into three parts for further investigation: 1) mixture of naphthenes and paraffins; 2) unsaturated hydrocarbons; 3) aromatic hydrocarbons. The yields of the narrow fractions and their group composition, obtained on the basis of the chromatographic data, are shown in Table 3. Data are cited below on the investigation of the aromatic hydrocarbons of the gasolines under study. After chromatography of the narrow fractions, the aromatic portion was distilled over metallic sodium and then investigated fractionally by the Raman spectra method. The results of the analysis are shown in Table 4.

Examination of the data of Tables 3 and 4 shows that the total yield of aromatic hydrocarbons for G-12 is twice that for G-11, and five times that for G-2. The principal aromatic hydrocarbons of G-12, in descending order, are: pseudocumene (27% of the total aromatics and 8.2% on the IBP-175° gasoline), toluene (respectively 18 and 5.4%), m-xylene (14 and 4.2%), ethylbenzene (10 and 3.0%), and p-xylene (7.8 and 2.4%). The first four of these hydrocarbons account for 69% of the total aromatics up to 175°. For G-11: toluene (30 and 4.6%, benzene (18 and 2.8%), m-xylene (9 and 1.4%), and ethylbenzene (also 9 and 1.4%); the four account for 66% of the total. For G-12: m-xylene (17 and 1.02%), toluene (14 and 0.94%), pseudocumene (13 and 0.87%), and ethylbenzene (11 and 0.73%); the four account for 55% of the total. It should be noted in addition that

TABLE 2. Hydrocarbon Composition of Fractions of Cracked Gasolines up to 60°

Hydrocarbons	Content, wt. %					
	gasoline 12		gasoline 2		gasoline 11	
	on IBP-60° fr.	on IBP-150° fr.	on IBP-60° fr.	on IBP-150° fr.	on IBP-60° fr.	on IBP-150° fr.
1	2	3	4	5	6	7
Ethane + ethylene	Traces	Traces	0.13	0.01	0.29	0.03
Propane + propylene	0.12	0.03	0.32	0.04	Not found	
2-Methylpropane	4.59	1.23	0.48	0.05	0.16	0.01
n-Butane	1.49	0.40	5.86	0.63	2.45	0.23
2-Methylpropene	3.46	0.93	4.51	0.49	3.10	0.28
n-Butenes	6.59	1.76				
3-Methylbutene-1	Traces	Traces	Traces	Traces	1.62	0.15
2-Methylbutane	36.4	9.78	11.1	1.20	7.36	0.68
Pentene-1	0.54	0.14	7.15	0.77	7.69	0.71
2-Methylbutene-1	1.69	0.46	5.23	0.55	6.14	0.56
Isoprene	Not found		0.14	0.01	0.32	0.03
Ethylcyclopropane	"		Traces	Traces	Traces	Traces
n-Pentane	0.32	0.09	25.0	2.68	19.9	1.83
Methylcyclobutane	Not found		Traces	Traces	Not found	
trans-Pentene-2	2.57	0.69	2.23	0.24	3.76	0.35
cis-Pentene-2	2.37	0.64	1.75	0.19	2.01	0.19
2-Methylbutene-2	15.1	4.06	7.93	0.85	10.0	0.92
1-Methylcyclobutene-1	Not found		Traces		Not found	
3,3-Dimethylbutene-1	0.09	0.02	Not found		Not found	
Piperylene	Not found		Not found		Traces	
Cyclopentene	1.16	0.31	0.82	0.09	3.66	0.34
Cyclopentane	++	++	3.98	0.43	7.23	0.67
2,2-Dimethylbutane	Not found		Not found		Traces	
4-Methylpentene-1	++	++	7.53	0.81	12.0	1.11
3-Methylpentene-1	++	++	0.58	0.06	0.40	0.03
2,3-Dimethylbutene-1	++	++	0.58	0.06	0.39	0.04
cis-4-Methylpentene-2	Not found		0.57	0.06	Not found	
1,3-Dimethylcyclobutane	Not found		Not found		Traces	
2,3-Dimethylbutane	4.7	1.86	3.05	0.32	3.55	0.33
trans-4-Methylpentene-2	Traces		1.78	0.19	0.79	0.07
2-Methylpentane	8.6	2.32	7.48	0.81	5.53	0.51
Traces and quantitatively uninterpreted hydrocarbons	9.3	2.76	2.41	0.26	2.55	–
Total $C_2 - C_6$	100.0	26.88	100.0	10.77	100.0	9.24
Paraffins $C_2 - C_6$	56.20	15.11	53.39	5.74	39.24	3.62
Including:						
Normal structure	1.93	0.52	31.29	3.36	22.64	2.06
Branched	54.27	14.59	22.10	2.38	< 16.60	< 1.53
Cycloparaffins C_5	++	++	3.98	0.43	7.23	0.67
Olefins $C_3 - C_6$	32.35	8.70	39.98	4.28	51.84	4.44
Including:						
Normal structure	13.71	3.23	11.66	1.26	> 16.56	> 1.53
Branched	18.64	5.47	> 28.32	> 3.02	> 31.62	> 2.91
Cycloolefins	>1.16	> 0.31	< 0.82	> 0.09	< 3.66	< 0.34

TABLE 3. Yield and Group Composition of Narrow Fractions of Gasolines 12, 2, and 11 Taken up to 175°

Fraction	Cut points, °C	Gasoline 12				Gasoline 2				Gasoline 11			
		yield on IBP-175° gasoline, wt. %	group* composition of fractions, wt. %			yield on IBP-175° gasoline, wt. %	group* composition of fractions, wt. %			yield on IBP-175° gasoline, wt. %	group* composition of fractions, wt. %		
			naphthenes & paraffins	unsaturates	aromatics		naphthenes & paraffins	unsaturates	aromatics		naphthenes & paraffins	unsaturates	aromatics
I—VI	IBP-60	21,2	56	44	—	8,3	57	43	—	7,3	46	54	—
VII	60—95	22,3	57	38	5	18,9	49	50	1	23,2	37	50	13
VIII	95—122	16,0	42	24	34	21,6	50	45	5	24,0	39	41	20
IX	122—150	19,4	29	10	61	28,5	51	39	10	24,6	37	44	19
X	150—175	21,1	36	4	60	22,7	50	37	13	20,9	42	38	20
VII—X	60—175	78,8	42	19	39	91,7	50	42	8	92,7	39	43	18

* Obtained by means of chromatographic separation of narrow fractions (see communication [1]).

TABLE 4. Aromatic Hydrocarbons Whose Presence has Been Established in Cracked Gasolines

Boiling point of fraction, °C	Hydrocarbons	Gasoline 12, yield, wt. %			Gasoline 2, yield, wt. %			Gasoline 11, yield wt. %		
		on aromat. fr.	on IBP-150° gasoline	on IBP-175° gasoline	on aromat. fr.	on IBP-150° gasoline	on IBP-175° gasoline	on aromat. fr.	on IBP-150° gasoline	on IBP-175° gasoline
60-95	Benzene	100	1,44	1,14	100	0,27	0,21	95	3,45	2,76
95-122	Toluene	100	6,86	5,42	85	1,21	0,94	97	5,77	4,57
	Ethylbenzene	25	3,75	2,98	25	0,94	0,73	30	1,76	1,39
122-150	p-Xylene	20	3,02	2,38	15	0,56	0,43	15	0,88	0,70
	m-Xylene	35	5,29	4,17	35	1,32	1,02	30	1,76	1,39
	o-Xylene	20	3,02	2,38	20	0,75	0,58	20	1,18	0,93
	1-Methyl-2-ethylbenzene	10	—	1,26	5	—	0,15	20	—	0,82
	1-Methyl-3-ethylbenzene	Traces	—	Traces	15	—	0,44	10	—	0,41
	1-Methyl-4-ethylbenzene	"	—	"	5	—	0,15	5	—	0,20
150-175*	Mesitylene	15	—	1,89	10	—	0,29	5	—	0,20
	n-Propylbenzene	Traces	—	Traces	10	—	0,29	10	—	0,41
	Pseudocumene	65	—	8,19	30	—	0,87	30	—	1,22
	Hemimellitene	5	—	0,63	15	—	0,44	10	—	0,41
	sec-Butylbenzene	Traces	—	Traces	Traces	—	Traces	—	—	—
	tert-Butylbenzene	—	—	—	"	—	"	—	—	

* The aromatic hydrocarbons from the 150-175° fraction of G-2 and G-11 contain 10% unsaturated hydrocarbons not yielding to identification. The cited aromatic concentrations for these fractions represent only a first approximation.

only in the gasoline from gas oil thermal cracking is there a high concentration of benzene, which reaches a minimum for the gasoline from thermal cracking of mazut.

The experimental part of the work was performed with the assistance of T. N. Buturlova and M. S. Lentovskaya.

SUMMARY

1. An investigation has been made on the individual hydrocarbon composition of three samples of carcked gasoline fractions boiling up to 60° and of the aromatic hydrocarbons of the 60-175° fractions of those same samples, which were produced from naphthenic-base crudes.

2. The data obtained attest to the high concentrations of hydrocarbons in the head fractions of cracked gasolines which can serve as raw material for petrochemical synthesis.

3. The concentrations of aromatic hydrocarbons such as pseudocumene, toluene, ethylbenzene, m-xylene, and p-xylene in the catalytically cracked gasoline considerably exceed their concentrations in the thermally cracked gasolines.

4. The data which have been presented show differences in the chemical composition of the gasolines investigated, in connection with differences in the chemical composition of the initial feedstock and the processing methods.

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EFFECTIVENESS OF VARIOUS CATALYSTS IN ALKYLATING PHENOL WITH ISOBUTENE

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The reaction of phenol alkylation with isobutene has been carried out with the aid of boron fluoride, compounds containing boron fluoride, $AlCl_2 \cdot HSO_4$, and with catalysts which have already found industrial application – sulfuric acid and aluminum chloride. The isobutene used for alkylation was prepared by catalytic dehydration of isobutanol on granular aluminum oxide at 380-400°. Analysis of the isobutene indicated 99% purity. The substance alkylated, phenol, had m. p. 41° and $n^{45}D$ 1.5401.

The method of alkylation was as follows: A 250 ml glass three-necked flask was charged with 94 g (1 mole) of phenol and 1.5 g of catalyst (1.6% of the phenol weight), and 56 g (1 mole) of isobutene from a gas-holder was fed at 4-5 liters/hr through a calcium chloride drier into the well-stirred reaction mixture. The completeness of isobutene absorption was controlled on the basis of escape of unreacted gas, which was collected in a second gas-holder, and by determining the increase in weight of the reaction mixture. The reaction was conducted at 100°; the reaction temperature was maintained within ± 0.5° by means of a contact thermometer.

In the alkylation of phenol by isobutene with various catalysts the reaction was conducted at 100° with a 1:1 molar ratio of phenol to isobutene and with catalyst quantity 1.6% of the phenol charge.

After completing the reaction, the mixture was washed several times with water to remove the catalyst and phenol. The quantity of unreacted phenol was determined by the bromide-bromate method. The oily crystals of p-tert-butylphenol which were obtained after treating the mixture with water were filtered on a glass filter under slight vacuum.

The crystals obtained on the filter were treated 3-4 times with 30-40 ml portions of cold petroleum ether. The filtrate was collected and dried, and the petroleum ether was distilled off. The residue represented oily crystals of p-tert-butylphenol, which were transferred to a glass filter where a thick oily liquid was separated from them on cooling. This liquid was cooled; if crystals of the alkylphenol precipitated, they were again cooled and subjected to filtration. The filtration process was performed until no separation of crystals was observed in the cooled oily liquid. The impure crystals which were obtained each time were treated as described above. The purified p-tert-butylphenol had m. p. 96°, mol. wt. 148, OH 10.9%. Literature data [1]: m. p. 98°, OH 11.32%, mol. wt. 150.12. Calculated: OH 11.32%, mol. wt. 150.12. The oily layer, from which p-tert-butylphenol no longer separated, had $n^{20}D$ 1.5142, OH 10.2%, and mol. wt. 174.1.

The over-all data on the investigation of the phenol alkylation reaction with isobutene at 100° and with additional 30 min mixing of the resulting reaction mixture at 120°, with various catalysts, are presented in Table 1. The boron fluoride catalyst was introduced into the flask in the form of a saturated solution in phenol. At 20-25°, 47 g of boron fluoride was added to 100 g of phenol.

From the data shown in Table 1 it follows that phenol is alkylated with isobutene most successfully in the presence of the catalysts containing boron fluoride, in comparison with the other catalysts under investigation. Under comparable conditions the experiments carried out with $H_3PO_4 \cdot BF_3$ and BF_3 gave p-tert-butylphenol yields of 81 and 83% respectively, while with $AlCl_3$ it reached only 70%. The yield of liquid products in alkylating phenol by means of $H_3PO_4 \cdot BF_3$ and BF_3 (14 and 12%) is lower than with $AlCl_3$ (24%). The increase of p-tert-butylphenol yield in the case of the catalysts containing boron fluoride occurs at the expense of a decrease in the formation of liquid products. The composition and method of investigating the liquid products of the phenol–isobutene alkylation are cited below.

From what has been stated, it follows that of the phenol–isobutene alkylation catalysts under investigation the most effective in the direction of p-tert-butylphenol formation are the complex of boron fluoride with orthophosphoric acid and especially boron fluoride. Therefore, as the next stage of the investigation, the effect of various factors on the boron fluoride catalyzed reaction was ascertained (catalyst quantity, temperature, ratio of reactants). The results of the investigation of catalyst quantity effect on the reaction are shown in Table 2.

TABLE 1. Comparative Data on Alkylation of Phenol by Isobutene with Various Catalysts (temperature 100°, 1:1 molar ratio of phenol to isobutene)

Catalyst	Composition of reaction mixture, %			Yield of reaction products, % theor.		
	phenol	p-tert-butylphenol	liquid products	p-tert-butylphenol	liquid products	total
$H_3PO_4 \cdot BF_3$	4,0	81,0	15,0	81	14	95
BF_3	4,2	83,0	12,8	83	13	96
$AlCl_3$	4,1	71,2	24,7	70	24	94
H_2SO_4*	24,7	56,7	18,6	65	19	84
$AlCl_2 \cdot HSO_4$*	38,6	50,7	10,7	51	11	62

* Optimum catalyst quantity under the given alkylation conditions was 75 g for (75%) H_2SO_4 and 4.5 g for $AlCl_2 \cdot HSO_4$.

TABLE 2. Effect of Catalyst Quantity on Composition and Yield of Reaction Products (temperature 100°, 1:1 molar ratio of phenol to isobutene)

Catalyst quantity		Composition of reaction mixture, %			Yield, % theor.		
g	% of phenol wt.	phenol	p-tert-butylphenol	liquid products	p-tert-butylphenol	liquid products	total
0,38	0,4	11,5	42,5	46,0	40	43	83
0,75	0,8	4,3	78,7	17,0	78	17	95
1,50	1,6	4,2	83,0	12,8	83	10	93
4,50	4,8	3,6	85,3	12,1	85	9	94
15,00	16,0	4,0	80,0	10,0	80	16	96

From these data it is evident that at the minimum quantity of boron fluoride catalyst (0.4%) the interaction of phenol and isobutene goes mainly toward liquid product formation, the yield of which reaches 43%. In this case the yield of p-tert-butylphenol is only 40%. An increase of catalyst quantity of 0.8% sharply increases the yield of p-tert-butylphenol to 78%, correspondingly decreasing the liquid product yield to 17%. An increase of catalyst quantity to 4.8% increases the yield of the desired product (p-tert-butylphenol) by 8-10%. If the catalyst quantity is is brought to 16%, then the opposite picture is observed – a decrease of the p-tert-butylphenol yield. In all probability such a relationship in the yields can be explained by the fact that with a small quantity of catalyst the rate of formation of ether products is greater than the rate of alkylation to form p-tert-butylphenol. It is well known that isobutene possesses a high capability for polymerization, and a large quantity of catalyst favors this reaction; therefore, in our case when alkylating with a large quantity of catalyst (16%), isobutene polymers appear.

Investigation of the liquid products of the boron fluoride catalyzed phenol–isobutene alkylation shows that they are a mixture of p-tert-butylphenol, o-tert-butylphenol, di-tert-butylphenol, tert-butyl ether of phenol, tert-butyl ether of tert-butylphenol, and isobutene polymers. The ratio of components of the mixture depends on the reaction conditions. We investigated in detail only the composition of the liquid products obtained with boron fluoride at a 1:1 molar ratio of phenol to isobutene, temperature 100°, and with additional 30 minute stirring of the reaction mixture at 120°.

The method of investigation consisted of the following: The liquid products of identical experiments (identical $n^{20}D$) were mixed together and treated several times with 10% potassium hydroxide solution. The alkaline layers were separated from the oily layers, combined, and treated with hydrochloric acid to liberate the phenols. The latter were washed with water to neutral reaction, dried over potassium carbonate, and distilled. The alkali-insoluble products were also washed with water to neutral reaction, dried, and fractionated.

Fractions were recovered from the alkaline solution with b. p. 76-100° (4 mm), 100-105° (4 mm), and 105-110° (4 mm); on standing, these fractions precipitated crystals, which were filtered off with cooling and, after recrystallization from water* (petroleum ether) had m. p. 98-99° and OH 11.6%, which corresponds to p-tert-butylphenol. The quantitative determination of hydroxyl groups was carried out by the method of Chugaev–Tserevitinov. The filtrates of these fractions were collected, combined, and fractionated at 4 mm Hg. As a result of distillation of the filtrates of the above-cited fractions, there were recovered fractions with b.p. 215-220° (n_D^{20} 1.5162, mol. wt. 151, d_4^{20} 0.9786, OH 11.11%), b.p. 220-240° (after recrystallization had m.p. 99°, OH 11.28%), b.p. 240-260° (n_D^{20} 1.5026, mol. wt. 204, OH 8.15%), and a fraction boiling above 260°. The yield of the intermediate fractions (b.p. up to 215° and boiling above 260°) was about 6% of the initial product. These fractions were not analyzed, because of their small quantity. The yields based on initial product were: b.p. 215-220° ~8%, b.p. 220-240° 26%, b.p. 240-260° 60%, and fraction above 260° ~2%.

A comparison of the physicochemical constants of the fractions obtained with the literature values of these constants for o-tert-butylphenol and p-tert-butylphenol shows that the 215-220° fraction represents fairly pure o-tert-butylphenol (literature data [2]: b. p. 217-220°, $n^{20}D$ 1.5160, OH 11.3%, d^{20}_4 0.9783), and the 220-240° fraction is p-tert-butylphenol of 90% purity. Literature data [1]: m. p. 98-99°, OH 11.32%, mol. wt. 150.12. The 240-260° fraction, to all appearances, represents a mixture of isomers of di-tert-butylphenol. The over-all yield of p-tert-butylphenol from the liquid products constituted 4.9%, o-tert-butylphenol 1.8%.

The following fractions were recovered from the alkali-insoluble products: b. p. 220-240° (yield 17%, $n^{20}D$ 1.5047, mol. wt. 152, OH 0%), b. p. 240-260° (yield 80%, $n^{20}D$ 1.5025, mol. wt. 208.4, OH 8.75%), and a fraction boiling above 260° (yield 3%). The 220-240° fraction represents the tert-butyl ether of phenol. Literature data [3]: b. p. 90° (32 mm), $n^{20}D$ 1.4881. The 240-260° fraction represents di-tert-butylphenol. Literature data [2]: m. p. 36.5°, b. p. 147° (30 mm). The fraction boiling above 260° was not analyzed. The over-all yield of the tert-butyl ether of phenol from the liquid reaction products, in percent of theoretical (on p-tert-butylphenol) constitutes 2%, and di-tert-butylphenols 9.1%.

The following series of experiments was conducted for the purpose of ascertaining the effect of temperature on yield of reaction products and composition of the reaction mixture. The data obtained are shown in Table 3.

TABLE 3. Effect of Temperature of Experiment on Composition and Yield of Reaction Products

Temperature of experiment, °C	Comp. of reaction mixture, %			Yield, % theor.		
	phenol	p-tert-butylphenol	liquid products	p-tert-butylphenol	liquid products	total
50	7,5	31,3	61,2	30	58	88
100 *	4,7	70,0	25,3	70	26	96
100 **	4,6	82,0	13,4	82	13	95
100 ***	4,2	83,0	12,8	83	13	96

* Heating was continued until termination of isobutene feed.

** After terminating isobutene feed, the reaction mixture was stirred 30 minutes more at 100°.

*** After terminating isobutene feed (at 100°), the reaction mixture was stirred 30 minutes at 120°.

The experiments carried out to ascertain the effect of temperature on composition and yield of reaction products show that the optimum temperature is 100°, and additional mixing (after terminating the isobutene feed) for

* As in russian original, but use of water for recrystallization of these particular substances seems unlikely.

30 minutes at 100-120°. In this case the yield of p-tert-butylphenol reaches a maximum value of 82-83%, and the liquid products a minimum value of 12-13%. The liquid products obtained under these conditions are a mixture of several compounds: p-tert-butylphenol (28%), o-tert-butylphenol (10%), di-tert-butylphenol (51%), and p-tert-butyl ether of phenol (11%).

The liquid products recovered from the reaction mixture obtained in the 50° phenol–isobutene alkylation contain a considerable quantity of isobutene polymers (~25%), along with some of the products indicated previously. The composition of these liquid products is as follows: p-tert-butylphenol 25%, other butylphenols (in all probability a mixture of di-tert-butylphenols and o-tert-butylphenol) 13%, tert-butyl ether of phenol 42%, and isobutene polymers 20%.

Investigation of the effect of phenol–isobutene molar ratio on the yield and composition of reaction products shows (Table 4) that on increasing the phenol–isobutene ratio from 1:1 to 2:1 the yield of p-tert-butylphenol is increased from 83 to 88%. No unsaturated hydrocarbons were found in the reaction products obtained at 2:1 molar ratio of phenol to isobutene. In this case the yield of di-tert-butylphenol is also decreased (1.5%).

TABLE 4. Effect of Phenol–Isobutene Molar Ratio on Composition and Yield of Reaction Products (BF_3 catalyst)

Molar ratio of phenol to isobutene	Composition of reaction mixture, %			Yield, % theor.		
	phenol	p-tert-butyl phenol	liquid products	p-tert-butyl-phenol	liquid products	total
1:0.5	41.4	53.0	5.6	88	9	97
1:1.0	4.6	80.0	15.4	83	13	96
1:2.0	0	23.4	76.6	32	–	–

The liquid products obtained at a 1:2 molar ratio of phenol to isobutene contain p-tert-butylphenol (8%), di-tert-butylphenol (75%), and the tert-butyl ether of p-tert-butylphenol (17%).

SUMMARY

1. A number of catalysts have been investigated in the phenol–isobutene alkylation reaction under comparable conditions, these catalysts including BF_3, $H_3PO_4 \cdot BF_3$, $AlCl_3$, H_2SO_4, and $AlCl_2 \cdot HSO_4$; it was shown that boron fluoride, taken in 0.8-1% quantity, is the most active catalyst and gives the highest yield of p-tert-butylphenol.

2. An investigation has been made of the effect of various factors on alkylate yield and composition in phenol–isobutene alkylation with boron fluoride. The yield of p-tert-butylphenol reaches 78-88% of the theoretical.

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CONTACT CATALYTIC CONVERSIONS OF C_{11}–C_{18} n-ALKANES UNDER HYDROGEN PRESSURE IN A FLOW SYSTEM

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In connection with the presence of a considerable quantity of normal-structure alkanes in certain crudes, the problem of exploring conditions for their catalytic isomerization is acquiring definite interest. Nevertheless, granting that a very great number of studies have been devoted to investigating the isomerization reaction of the lower alkanes occurring in gasolines, until very recently the attention given to studying this reaction in the higher molecular weight kerosene-range alkane series has been clearly inadequate. To elucidate the mechanism of the catalytic isomerization of alkanes, Petrov, Sergienko, and co-workers [1, 2] investigated the isomeric conversions of C_6–C_8 and C_{12}–C_{16} alkanes. The studies of Ciapetta and Hunter [3] and those of Hettinger and co-workers [4] were devoted to an investigation of the contact conversions of C_6–C_9 normal alkanes.

We decided to investigate the conditions of catalytic isomerization and cyclization of the individual C_{11}–C_{18} normal alkanes, which we isolated in pure form from the 190-350° fraction of Sokolova Gora and Mirzaan crudes [5, 6]. Certain data from earlier studies of one of the authors [7-10] were utilized in selecting suitable conditions for carrying out the isomerization and cyclization of these hydrocarbons. As a result of our investigation it was found that, in the presence of 0.5% Pt on gumbrine [floridin-type bleaching clay] and 0.5% Pd on gumbrine at 450° and 30 atm hydrogen pressure in a flow system, the original n-alkanes are extensively converted along the lines of isomerization, cyclization, dehydrocyclization, and partial hydrocracking. The result of these conversions is the formation of a mixture of hydrocarbons having a lower freezing point and an increased heat of combustion. It should be especially noted that in the case of the conversions of n-heptadecane and n-octadecane we have demonstrated for the first time the possibility of their direct catalytic polycyclization to the condensed system of phenanthrene and other polycyclics.

Up to the present, the only known observations have been on the closing of an alkylbenzene side chain with not less than four atoms, forming the condensed system of naphthalene, as carried out by Moldavskii [11], Karzhev [12], and then by Nametkin, Khotimskaya, and Rozenberg [13]. Such a cyclization was demonstrated most conclusively by Sergienko [14] for the example of the conversion of isoamylbenzene to β-methylnaphthalene in the presence of dehydrogenation catalysts. The formation of naphthalene was also observed in the catalytic dehydrocyclization of n-decane by Karzhev [12], Komarevsky [15], and Rozenberg [16].

EXPERIMENTAL

We carried out the experiments in a flow unit under hydrogen pressure, permitting sufficiently accurate regulation of temperature, pressure, and hydrocarbon feed rate to the catalyst. The flow plan of the unit was presented in our earlier work [17, 18]. For the case of contact catalytic conversions of n-tridecane and cetane in the presence of 0.5% Pt supported on alumina, we had established the optimum conditions for reforming these higher alkanes [18], which were taken as the basis of carrying out further investigation of the other individual hydrocarbons. The initial alkanes were fed to the reaction zone at a space velocity of 0.5 hr^{-1} under 30 atm pressure with a 3:1 molar ratio of hydrogen to hydrocarbon. The catalysts used were 0.5% Pt and 0.5% Pd on alumina and 0.5% Pt and 0.5% Pd on a activated natural aluminosilicate (gumbrine), whose properties we had described earlier [19]. The catalyst volume was 100 ml in all experiments. All experiments were conducted at 450°; in each experiment we took up to 100 g of hydrocarbon.

The results of the investigation of the total liquid products are presented in Table 1. By comparing the data shown in Table 1 pertaining to the conversions of cetane with the results obtained in experiments on contacting this hydrocarbon with gumbrine [18], it is evident that the presence of 0.5% Pt and 0.5% Pd has a substantial influence on the degree and character of the alkane conversions. This influence of the indicated group VIII metals is manifested in a three- to fourfold decrease of hydro-cracking gases, in a two- to threefold increase of the aromatic hydrocarbon yield, and in the formation of a considerable quantity of cyclanes and products of isomerization, as a result of which the freezing point of the total liquid products is lowered sharply and their heat of combustion is increased.

TABLE 1. Properties of Products Obtained from Normal Alkanes $C_{11}H_{24}$–$C_{18}H_{38}$ in Conversions on Various Catalysts at 450° and 30 atm H_2 Pressure

Exp. No.	Catalysts	Yield of total liquid product, wt. %	Properties of total liquid products					
			n_D^{20}	d_4^{20}	freezing point, °C (appearance of 1st cryst.)	Q_1^u, kcal/kg	content of aromatic hydrocarbons, %	total % fraction boiling below 100°
			n-$C_{11}H_{24}$					
19	0,5% Pt—Al_2O_3	93,2	1,4200	0,7464	—45,0	11192	10,5	5,2
20	0,5% Pd—Al_2O_3	94,3	1,4190	0,7439	—42,0	11307	9,0	4,2
21	0,5% Pt— gumbrine	89,4	1,4050	0,6984	—62,0	12085	18,0	17,8
22	0,5% Pd— gumbrine	90,3	1,4076	0,6997	—60,0	10031	17,0	16,0
			n-$C_{12}H_{26}$					
23	0,5% Pt—Al_2O_3	93,3	1,4240	0,7519	—27,5	11128	13,5	5,7
24	0,5% Pd—Al_2O_3	95,0	1,4227	0,7494	—27,0	11797	10,5	4,0
25	0,5% Pt— gumbrine	89,9	1,4058	0,7033	—30,0	11831	18,0	17,8
26	0,5% Pd— gumbrine	91,4	1,4030	0,7151	—48,0	11038	18,5	16,5
			n-$C_{13}H_{28}$					
27	0,5% Pt—Al_2O_3	94,5	1,4290	0,7581	—28,0	11784	10,0	8,5
28	0,5% Pd—Al_2O_3	94,5	1,4278	0,7564	—36,5	11473	15,5	11,0
29	0,5% Pt— gumbrine	92,4	1,4230	0,7487	—47,5	10727	18,0	28,9
30	0,0% Pd— gumbrine	92,1	1,4239	0,7498	—44,0	11030	17,0	24,2
			n-$C_{14}H_{30}$					
31	0,5% Pt—Al_2O_3	93,5	1,4308	0,7682	—25	11015	12,0	10,9
32	0,5% Pd—Al_2O_3	93,6	1,4303	0,7678	—32,5	11126	10,5	12,0
33	0,5% Pt— gumbrine	91,9	1,4282	0,7601	—38	11124	14,0	17,3
34	0,5% Pd— gumbrine	92,8	1,4195	0,7450	—29	10894	11,0	34,1
			n-$C_{15}H_{32}$					
35	0,5% Pt—Al_2O_3	95,50	1,4338	0,7655	—16	10794	10,6	9,3
36	0,5% Pd—Al_2O_3	94,45	1,4307	0,7692	—14,5	11299	11,0	7,9
37	0,5% Pt— gumbrine	90,00	1,4180	0,7296	—32,5	10833	18,5	31,5
38	0,5% Pd— gumbrine	92,70	1,4230	0,7307	—17	11643	18,5	30,2
			n-$C_{16}H_{34}$					
39	0,5% Pt—Al_2O_3	93,70	1,4340	0,7612	—23	11327	11,5	9,1
40	0,5% Pd—Al_2O_3	94,63	1,4340	0,7703	—14,5	11295	16,0	6,1
41	0,5% Pt— gumbrine	91,93	1,4268	0,7338	—27,5	11165	12,0	31,0
42	0,5% Pd— gumbrine	89,90	1,4080	0,7165	—16,5	11703	13,0	35,2
			n-$C_{17}H_{36}$					
43	0,5% Pt—Al_2O_3	94,40	1,4390	0,7809	— 4	11430	10,8	6,6
44	0,5% Pd—Al_2O_3	92,32	1,4389	0,7784	— 2	11934*	11,0	6,8
45	0,5% Pt— gumbrine	88,51	1,4162	0,7253	—26	10793	23,5	27,5
46	0,5% Pd— gumbrine	89,42	1,4030	0,7024	—24	11493	24,0	32,8
			n-$C_{18}H_{38}$					
47	0,5% Pt—Al_2O_3	93,41	1,4420	0,8115	1	11417	11,5	5,6
48	0,5% Pd—Al_2O_3	93,93	1,4380	0,7795	2	11351	12,0	3,6
49	0,5% Pt— gumbrine	89,84	1,4252	0,7294	—14,5	11285	18,0	28,0
50	0,5% Pd— gumbrine	90,58	1,4262	0,7200	—10,5	11358	16,0	31,2

* Gross (upper) heat of combustion.

After removal of a head fraction (boiling up to 100°) from the total liquid products in a 75-theoretical-plate column, aromatic hydrocarbons were recovered from the remaining portion by chromatographic adsorption on Type ASM silica gel. Then the desorbed mixture of aromatic hydrocarbons was fractionated in a 25-theoretical-plate column in a nitrogen atmosphere. Toluene and xylenes were found in the fractions boiling up to 150°, on the basis of physicochemical constants and data of optical analysis. At the same time, it was noted that the product fractions obtained from the alkane conversions on Pt–Al_2O_3 and Pd–Al_2O_3 contained not more than 3.5% toluene and xylenes, whereas the corresponding fractions from the experiments with Pt and Pd deposited on gumbrine contained these hydrocarbons in quantity up to 9%. The total content of aromatic hydrocarbons in the total liquid products in the experiments conducted with Pt–gumbrine and Pd–gumbrine varied between 12.1 and 24%, while with Pt–Al_2O_3 and Pd–Al_2O_3 the aromatics constituted only 9.1 to 17.3%. This circumstance points out the ability of gumbrine to initiate the aromatization reaction.

TABLE 2. Properties of Fractions Recovered by Chromatographic Adsorption on Al_2O_3 from Mixtures of Aromatic Hydrocarbons Boiling Above 150°

Fraction No.	Column I					Column II				
	quantity, g	b.p. °C at 731 mm Hg	n_D^{20}	d_4^{20}	m.p. of picrate, °C	quantity, g	b.p. °C at 733 mm [Hg]	n_D^{20}	d_4^{20}	m.p. of picrate, °C
II	Did not luminesce					4,9	292—293	1,6383	1,0789	116—118
III	3,8	290—295	1,6185	1,0250	112—113	7,3	275—180	1,6323	1,0630	184—186
IV	10,1	289—290	1,5910	0,9940	103—105	8,6	268—269	1,6179	1,0228	109—112
V	11,2	273—275	1,5289	0,9055	89—91	16,1	266—268	1,5070	0,8785	98—100
VI	9,2	266—268	1,4908	0,8666	—	26,6	253—260	1,4870	0,8185	—

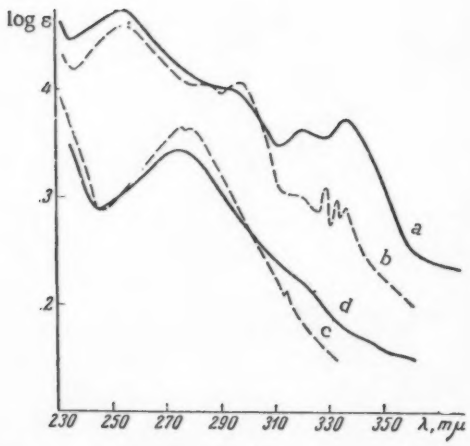


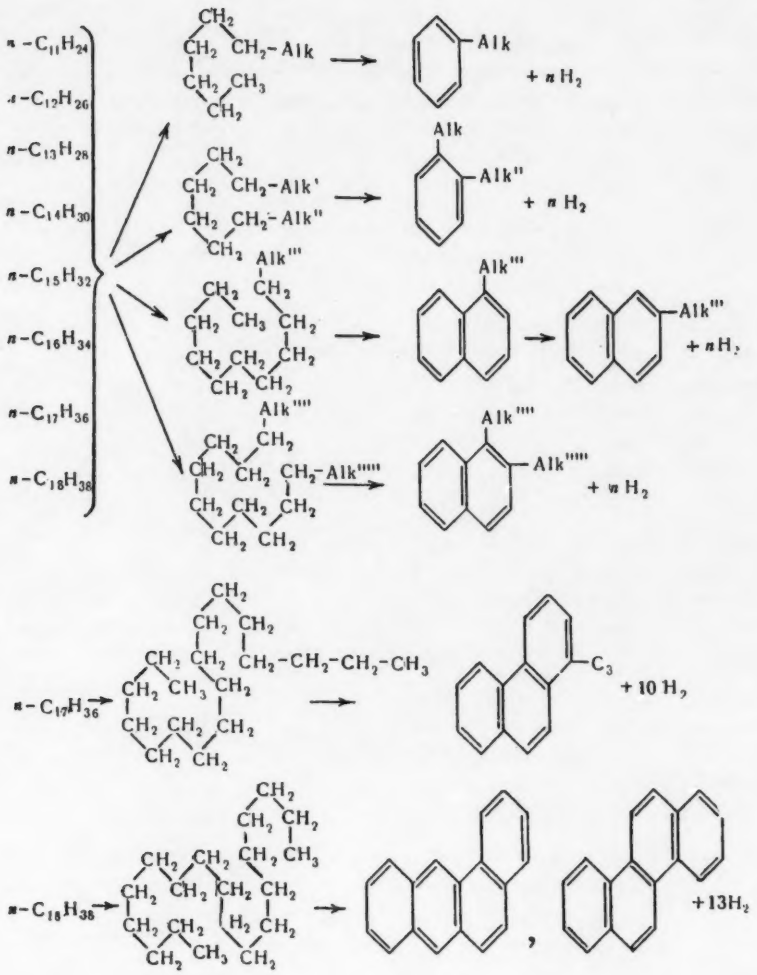
Fig. 1. UV spectra of fractions II-III and IV in solution of 2,2,4-trimethylpentane: a) Fractions II-III; b) phenanthrene; c) α-methylnaphthalene; d) fraction IV.

The aromatic hydrocarbons boiling above 150° had a bluish-green fluorescence, especially those obtained in experiments with the alkanes C_{16} and higher. Therefore, the aromatic hydrocarbons obtained in the conversions of n-heptadecane and n-octadecane on Pt–Al_2O_3 and Pd–Al_2O_3 (experiments 43, 44, 47, and 48) on the one hand, and on Pt–gumbrine and Pd–gumbrine (experiments 45, 46, 49, and 50) on the other hand (see Table 1) were combined and subjected to chromatography in petroleum ether solution on activated alumina in two glass columns, each containing 200 ml of fine-grained Al_2O_3 (Table 2). On exposing them to 360 mμ ultraviolet light, the mixture of aromatic hydrocarbons (41.0 g) obtained in the experiments with Pt–Al_2O_3 and Pd–Al_2O_3 (column I) was separated into five zones, of which four zones luminesced with a pale violet to pale azure glow. The mixture of aromatic hydrocarbons (76.9 g) obtained in the experiments with Pt–gumbrine and Pd–gumbrine (column II) was separated into six zones, of which five (II-VI) had a pronounced luminescence: Zone II luminesced with a yellow-green glow, zone III pale azure, zone IV azure, zone V violet, and zone VI pale violet. Data are shown in Table 2 on the chromatographic investigation of the individual zones of columns I and II.

For the fractions II, III and IV recovered from column II, ultraviolet absorption spectra were taken on an SF-4 spectrophotometer in isooctane solution. A comparison of the spectra of different polycyclic aromatic hydrocarbons, as shown in Fig. 1, demonstrated that the spectrum of phenanthrene and its homologs (curve b) is the closest to the spectrum of the compounds of fractions II and III (curve a). The spectrum of fraction IV (curve d) shows the character of the absorption curve of α-methylnaphthalene (curve c).

The elemental analysis of fraction II was carried out, showing that its composition represents propylphenanthrene, probably with admixed chrysene or benzanthracene. Found for fraction II: C 92.03, 92.30; H 7.90, 7.86%. $C_{17}H_{16}$. Calculated: C 92.67; H 7.33%. $C_{18}H_{18}$. Calculated: C 92.25; H 7.75%.

In addition, a luminescence spectrum was taken for fraction II in the visible region in n-heptane solution. As is evident from the curve (Fig. 2), the maximum lies in the vicinity of $\lambda = 445$ mμ, which is characteristic for polycyclic aromatic hydrocarbons. Thus, the optical properties and elemental composition of fraction II point to the presence of alkylphenanthrenes with side groups $C_3 - C_4$, with admixed chrysene and benzanthracene. However, on the basis of the data obtained up to the present it is not possible to judge the nature and position of these groups. Probably the material of fraction II which has the pronounced yellow-green luminescence is a mixture of n-propyl and n-butyl phenanthrenes with admixed chrysene and benzanthracene. Proceeding from the sextet model of the Balandin multiplet theory, the formation of alkylbenzenes and condensed systems can be expressed by the following scheme:



Under the conditions which we adopted the yield of fraction II, consisting of homologs of phenanthrene, constituted ~ 3.5%. At present we are engaged in an investigation of the direct catalytic synthesis of condensed aromatic systems by polycyclization of the higher alkanes under conditions making it possible to obtain the aromatics in individual form with high yields.

After removing the aromatic hydrocarbon mixture consisted of cyclanes and isoalkanes. For determining six-membered cyclanes, the mixture was subjected to dehydrogenation catalysis by the Zelinskii method. After determining the six-membered cyclanes and removal of the aromatic hydrocarbons thereby formed, the remaining mixture consisted of five-membered cyclanes and isoalkanes. The determination of five-membered cyclanes was carried out by isomerizing them to six-membered cyclanes in the presence of anhydrous aluminum chloride [20] and then

dehydrogenating them catalytically. The results obtained are shown in Table 3. For the isoalkanes which remained, physicochemical constants and also freezing points were determined; all of the freezing points were within the limits of −65 to −75°. In addition, the structure of the isoalkanes was investigated by means of infrared spectroscopy (IKS-11 with NaCl and LiF prisms) [21]; the predominating structures were iso-forms with a tertiary carbon atom (absorption bands, 1170 med − 1140 med). In all of the spectra, there was also discovered one of the bands characterizing the skeletal vibrations of the quaternary carbon atom.

TABLE 3. Catalytic Conversion Products of $C_{11}H_{24}$–$C_{18}H_{38}$ n-Alkanes in the Presence of Pt and Pd Catalysts on Al_2O_3 and Gumbrine

Initial hydrocarbons	Exp. No.	Aromatic hydrocarbons	Five-membered cyclanes	Six-membered cyclanes	Isoalkanes	n-Alkanes	n-Alkanes with lower mol. wt. than original	n-Alkanes remaining without change	Degree of conversion
n-$C_{11}H_{24}$	19	12,0	2,0	3,0	39,5	36,7	11,7	25,0	75,0
	20	11,3	1,5	3,5	35,7	42,1	15,1	27,0	73,0
	21	20,5	3,2	5,7	52,1	7,9	3,4	4,5	95,5
	22	21,0	2,8	4,5	51,7	10,3	4,8	5,5	94,5
n-$C_{12}H_{26}$	23	15,8	2,3	3,4	33,6	36,2	13,6	22,6	77,4
	24	13,8	2,3	3,2	40,2	35,5	9,5	26,0	74,0
	25	24,0	3,0	4,5	54,2	4,3	1,1	3,3	96,7
	26	23,0	3,5	3,0	55,6	6,3	2,0	4,3	95,7
n-$C_{13}H_{28}$	27	11,6	6,3	6,5	28,6	41,5	21,7	19,8	80,2
	28	17,3	5,0	4,9	35,5	32,1	20,1	12,0	88,0
	29	19,4	5,8	9,5	45,9	13,3	10,7	5,1	94,9
	30	16,9	4,3	5,6	44,7	20,6	16,3	4,5	95,5
n-$C_{14}H_{30}$	31	14,4	3,9	6,2	40,7	29,5	20,9	8,6	91,6
	32	14,5	3,2	6,8	43,6	25,5	18,1	7,4	92,6
	33	15,9	3,5	11,2	48,2	15,2	12,5	2,7	97,3
	34	12,1	3,0	8,2	62,0	7,5	3,8	3,7	96,3
	35	13,6	2,1	3,0	23,6	50,9	40,4	10,5	89,5
n-$C_{15}H_{32}$	36	12,7	3,0	4,5	33,8	38,5	29,1	9,4	90,6
	37	17,2	2,1	4,1	47,9	21,6	18,1	3,5	96,5
	38	15,6	2,6	3,5	44,9	26,6	23,9	2,7	97,3
n-$C_{16}H_{34}$	39	13,1	5,2	6,6	47,7	21,0	11,0	10,0	90,0
	40	9,1	2,2	3,6	30,3	46,3	37,6	8,7	91,3
	41	12,2	2,3	4,2	50,7	21,9	18,0	3,9	96,1
	42	12,8	3,1	6,3	51,6	17,1	13,5	3,6	96,4
n-$C_{17}H_{36}$	43	10,7	4,0	5,5	27,9	47,8	38,3	9,5	90,5
	44	11,4	1,9	3,9	37,8	36,9	26,5	10,4	89,6
	45	21,0	2,2	4,3	47,5	16,1	13,5	2,6	97,4
	46	22,0	2,1	3,9	45,3	15,4	13,4	2,0	98,0
n-$C_{18}H_{38}$	47	13,5	2,7	3,9	24,4	47,1	39,4	7,7	92,3
	48	14,8	4,0	6,3	23,2	41,0	31,0	10,0	90,0
	49	17,0	2,0	3,7	43,5	26,4	22,1	4,3	95,7
	50	19,4	2,1	3,6	45,2	23,3	20,1	3,2	96,8

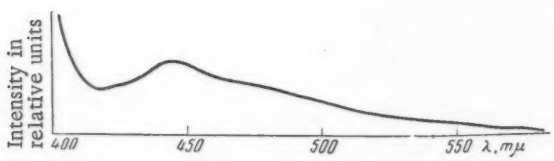


Fig. 2. Luminescence spectrum in the visible region for fraction II in n-heptane solution.

From the results of the completed investigation it is evident that the normal alkanes $C_{11}H_{24}$–$C_{18}H_{38}$ in the presence of the catalysts which we used, particularly in contact with Pt–gumbrine or Pd–gumbrine, undergo extensive conversions. Reactions of hydrogenolysis, isomerization, dehydrocyclization, polycyclization, and partial hydrocracking take place.

T. S. Shakarashvili took part in carrying out the experimental part of the work. The optical analysis was carried out by Yu. P. Egorov, for which the authors express great gratitude. The authors also thank A. N. Nikitina, who measured the luminescence spectrum.

SUMMARY

1. An investigation has been made on the catalytic conversions of C_{11}–C_{18} normal alkanes in the presence of 0.5% Pt–Al_2O_3, 0.5% Pd–Al_2O_3, 0.5% Pt–gumbrine, and 0.5% Pd–gumbrine, at 450° in a flow system under 30 atm hydrogen pressure.

2. The principal conversion of the indicated alkanes under these conditions is their isomerization, forming up to 62% isoalkanes, which leads to a 16-48.5° lowering of the freezing points of the liquid products obtained and to an increase of the heats of combustion on the average by 140 to 1240 kcal/kg.

3. The normal alkanes beginning with C_{16}, in the presence of 0.5% Pt–gumbrine, undergo conversions with the formation not only of products of hydrogenolysis, isomerization, and partial hydrocracking, but also of polycyclization products. Thereby, the phenanthrene, benzanthracene, and chrysene systems are formed.

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CONVERSIONS OF n-NONADECANE AND EICOSANE IN A FLOW SYSTEM OVER METAL OXIDE CATALYSTS UNDER HYDROGEN PRESSURE

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In one of the preceding studies of an example of the catalytic conversion of normal tridecane [1], and also of tetra-, penta- and hexadecanes [2] we found the optimum conditions for the isomerization and cyclization of these alkanes, which was based on an investigation of the conversion of normal alkanes the compositions of which varied from C_{11} to C_{18} [3]. As a result of a detailed study of the liquid products of catalysis that were obtained, it was shown that because under these conditions from 50 to 62% of isoalkanes are formed, there occurs an increase in the calorific value of from 140 to 1240 cal/kg, and a decrease in the solidification temperature of from 16-48.5°. We also found that under these conditions dehydrocyclization of the alkanes occurs, with the formation not only of monocyclic and bicyclic aromatic hydrocarbons, but also of condensed polycyclic systems.

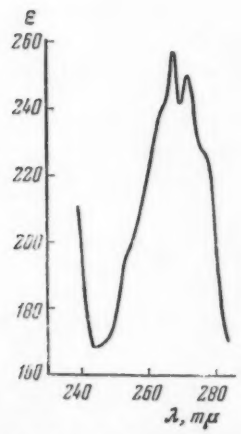


Fig. 1. UV spectra of combined fractions V and VI (experiment 58).

Up to the present, dehydrocyclization over oxide and platinum catalysts has only been studied carefully in the case of alkanes of comparatively simple structure which form benzene, toluene and xylene [4-6] or naphthalene [5, 7-11]. However, on the basis of Balandin's multiplet theory and the sextet model of dehydrogenation catalysis, one might expect that the higher normal alkanes, beginning with undecane, should form condensed aromatic hydrocarbons under favorable conditions for dehydrocyclization. And indeed, in our studies [12] we observed the direct cyclization of the higher alkanes with the formation of mono-, bi- and polycyclic hydrocarbons, which were identified by means of chromatographic, spectrographic and other analytical methods. This was reported in detail at the VIII Mendeleev Congress [13].

In order to continue these investigations further, and also in order to clarify certain peculiarities in the cyclization of individual hydrocarbons, we considered it advisable to study the contact-catalytic conversions of n-nonadecane and eicosane which occur in the gas-oil fraction of petroleum and have b. p. of 320-340°. The experiments were carried out in a flow system, a description of which was given in our previous papers [1, 14].

The following catalysts were used in the experiments: Pt and Pd – Al_2O_3, Pt and Pd on "gumbrin" (a natural aluminum silicate), whose composition and properties were given in one of our previous papers [2]. The alkanes were moved through the reaction zone at a volume velocity of 0.5 per hour under 30 atmospheres of hydrogen pressure, and with a molar ratio of hydrogen to hydrocarbon of 3:1. The volume of catalyst in all cases was 100 ml. All experiments were carried out at 450°.

The properties of the original alkanes and of the liquid products of catalysis, both before and after removing the light fraction boiling up to 100°, are shown in Table 1. Study of the liquid catalytic products was carried out by the methods described in our previous papers [1, 2, 12].

As can be seen from the data given in Table 1, as a result of catalytic conversion, normal alkanes form products of catalysis with increased calorific value Q_1^u, and with a decreased solidification point. It should be noted that these properties were more marked in the case of products of catalysis formed over Pt and Pd-"gumbrin" than of those formed over Pt and Pd on Al_2O_3.

TABLE 1. Properties of the Original Alkanes and of the Liquid Products of Catalysis Obtained by Their Catalytic Conversion

Original hydrocarbons	Properties of original hydrocarbons					Catalysts	Properties of products of catalysis						Properties of products of catalysis after removing light fraction with b.p. up to 100°				Amount of coke in the catalyst, % by wt.
	b.p. °C at 736 mm	d_4^{40}	n_D^{20}	F.p., °C (appear. of 1st crystal)	Q_1^u, Cal/kg		d_4^{20}	n_D^{20}	F.p., °C (appear. of 1st crystal)	aromatic hydrocarbons, vol. %	light fraction, b.p. to 100°, % by wt.	Q_1^u, Cal/kg	d_4^{20}	n_D^{20}	solidification point, °C (appearance of first crystal)	Q_1^u, Cal/kg	
$n\text{-}C_{19}H_{40}$	321—323	0,7862	1,4334 (40°)	31	10710	0,5% Pt—Al_2O_3	0,7884	1,4435	11,5	7,0	4,6	10975	0,7893	1,4443	13	10539	6,98
						0,5% Pd—Al_2O_3	0,7807	1,4420	2,0	14,0	5,67	10803	0,7899	0,4465	8,2	11063	3,14
						0,5% Pt—gumbrine	0,7225	1,4180	—5	16,5	30,9	11446	0,7753	1,4398	9	11006	2,14
						0,5% Pd—gumbrine	0,7025	1,4150	0,8	25,0	38,2	11037	0,7591	1,4331	7,8	11018	2,15
$n\text{-}C_{20}H_{42}$	334—337	0,7883	1,4348 (40°)	34,8	10421	0,5% Pt—Al_2O_3	0,7808	1,4421	0,7	14,5	5,35	11061	0,7930	1,4446	3,5	10860	6,48
						0,5% Pd—Al_2O_3	0,7784	1,4400	—2,2	13,0	6,89	11213	0,7884	1,4449	8,5	10917	3,66
						0,5% Pt—gumbrine	0,7102	1,4190	—12	15,0	36,8	11384	0,7636	1,4326	—6	10649	2,20
						0,5% Pd—gumbrine	0,7256	1,4185	—6	20,0	22,6	11088	0,7699	1,4370	6	11136	3,36

* Gross (upper) heat of combustion.

After removal from the products of catalysis of the light fraction boiling below 100° in a column with an effectiveness of 75 theoretical plates, the aromatic hydrocarbons were removed from the remainder by means of chromatographic adsorption on silica gel (ASM brand).

In the mixture of aromatic hydrocarbons obtained by the conversion of $n\text{-}C_{19}H_{40}$ and $n\text{-}C_{20}H_{42}$, unlike the aromatic hydrocarbons formed in the conversion of normal alkanes of the series $C_{11} - C_{18}$, no fraction boiling below 150° was found among the reaction products. The aromatic hydrocarbons that boiled above 150° had a yellowish-green fluorescence; they were studied chromatographically in a solution of petroleum ether in glass columns containing 200 ml of activated aluminum oxide. During chromatography the columns were illuminated by ultraviolet light with a wavelength of $\lambda = 360$ mμ. As a result some zones of different luminescence appeared, from which aromatic hydrocarbons were desorbed; their characteristics are shown in Table 2. Ultraviolet absorption spectra of all these narrow fractions were taken on an SF-4 spectrophotometer in a solution of n-heptane, and the infrared spectra were taken by the method worked out by Egorov [15].

The UV absorption spectra showed that fractions VI and V consist of a mixture of alkyl-, para- and metadialkylbenzenes. By means of infrared spectra the presence of an average of two CH_3 groups, and also of from eight to nine CH_2 groups in the side chains was determined (Fig. 1).

Results of the UV study of fraction IV are shown in Fig. 2, where the values of log ϵ are shown on the ordinate scale. As can be seen from the absorption curves, the peak in the 255 mμ region has the shape that is characteristic of diphenyl derivatives, while the other maximum in the 280-290 mμ region is characteristic of naphthalene derivatives. On the basis of this one may conclude that the given fraction contains naphthalene and diphenyl derivatives. The infrared spectrum showed two CH_3 groups and from five to six CH_2 groups as substitutents in side chains. This same fraction of aromatic hydrocarbons was treated with picric acid according to Nametkin's method [16] and α- and β-alkylnaphthalenes with m. p. 112-114° and 116-118° were found.

The combined fractions II-III were also subjected to analysis on an SF-4 spectrophotometer. The spectra of this fraction show that the most intense absorption band lies in the 255 mμ region. According to its form this band, apparently, is due to phenanthrene or to its alkyl derivatives which are the principal part of these fractions. The fractions also have bands in the 310-340 mμ region which, apparently, are due to chrysene or its derivatives. An approximate estimate of the content of alkylchrysenes is ~ 30%. However, in the spectra of fractions II-III the intensity of absorption in the 310-340 mμ region is greater than in the corresponding aromatic hydrocarbons. It is possible to assume that the reason for this deviation is an admixture of 1,2-benzanthracene or its alkyl derivatives, since the spectrum of benzanthracene is noted for its higher intensity. Thus, as a result of optical analysis, it is possible to conclude that fraction II-III contains condensed aromatic hydrocarbons. The UV spectrum of this combined fraction is shown in Fig. 3.

The luminescent spectrum of fraction II-III in a solution of heptane was also studied in the visible region, excited by illumination from a mercury lamp with λ = 360 mμ. All samples of fraction II-III luminesce most strongly in the 425-485 mμ region. In this range are found the luminescent spectra of solutions of such polycyclic hydrocarbons as 1,2-benzanthrene, perylene, benzperylene and the long wave part of the spectra of such hydrocarbons as phenanthrene, chrysene, pyrene, etc. Therefore the luminescense studies of these samples may be considered as a confirmation of the presence of polycyclic hydrocarbons of the same family (Fig. 4).

TABLE 2. Properties of Aromatic Hydrocarbons with b. p. >150°, which were Separated from the Liquid Products of Catalysis

Zones	Catalysts Pt and Pd on Al_2O_3					Pt and Pd on "gumbrin"			
	aromatic hydrocarbons	hydrocarbon content of products of catalysis, %	b. p., °C at 763 mm	$n^{20}D$	d^{20}_4	hydrocarbon content of products of catalysis, %	b. p., °C at 763 mm	$n^{20}D$	d^{20}_4
Original alkane n-$C_{19}H_{40}$									
II-III	Polycyclic	1.2	274-276	1.6590	1.0541	6.4	288-290	1.6690	1.1262
IV	Bicyclic	13.9	232-233	1.5560	0.9802	21.8	270-273	1.6310	1.0230
V-VI	Monocyclic	4.0	188-190	1.4666	0.8490	7.6	170-172	1.4960	0.8701
Original alkane n-$C_{20}H_{42}$									
II-III	Polycyclic	1.3	295-298	1.6610	1.1203	7.4	305-310	1.6567	1.2153
IV	Bicyclic	14.1	266-267	1.6203	0.9947	19.7	278-283	1.6424	1.0480
V-VI	Monocyclic	6.4	195-196	1.4796	0.8530	6.0	184-185	1.5010	0.8715

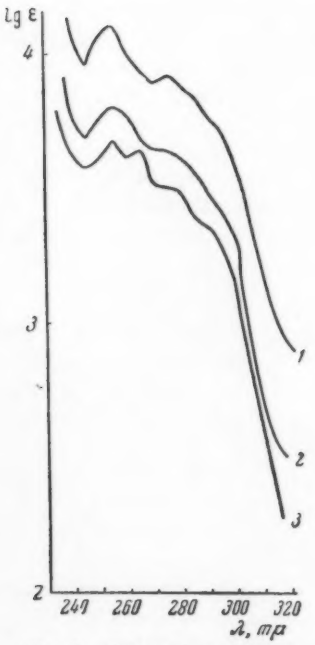
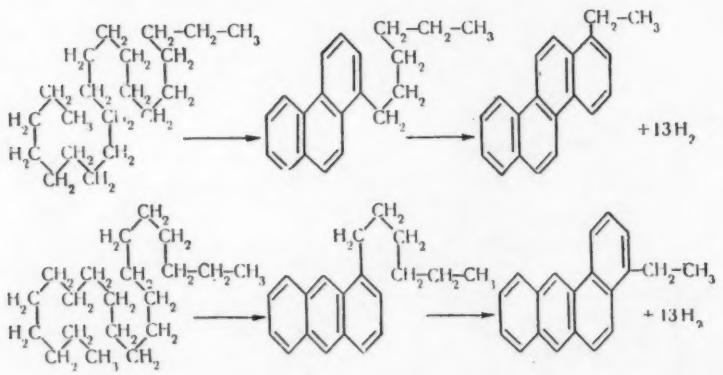


Fig. 2. UV spectra of fraction IV: 1) Experiment 58; 2) experiment 54; 3) experiment 55.

We also succeeded in separating crystalline substances with melting points of 135-136° and 163-165° from the combined fraction II-III. When illuminated by ultraviolet light of wavelength λ = 360 mμ the crystals luminesced brightly, giving off a greenish-blue color. These crystals are shown in Fig. 5. Thus, study of the narrow fractions of the aromatic hydrocarbons that were obtained shows the presence in them of mono- and polycyclic aromatic hydrocarbons.

Starting from the sextet model of Balandin's multiplet theory, the formation of condensed systems may be expressed in accordance with the following scheme:



The results of chromatographic analysis of a mixture of aromatic hydrocarbons are shown in Table 3.

After removal of the aromatic hydrocarbons from the products of catalysis by adsorption on silica gel, and of the normal alkanes by means of the carbamide

method, there remained a mixture of hydrocarbons consisting of cyclanes and isocyclanes. The content of six-membered and five-membered cyclanes was determined by the well-known Zelinskii method [17].

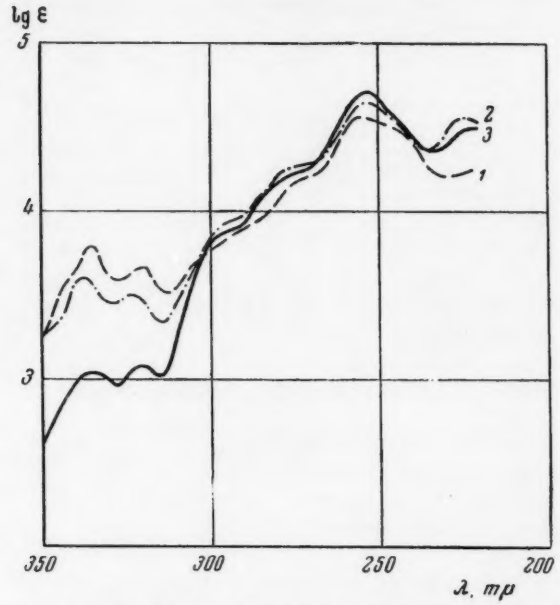


Fig. 3. UV spectra of the combined fractions II and III: 1) Experiment 58; 2) experiment 54; 3) experiment 55.

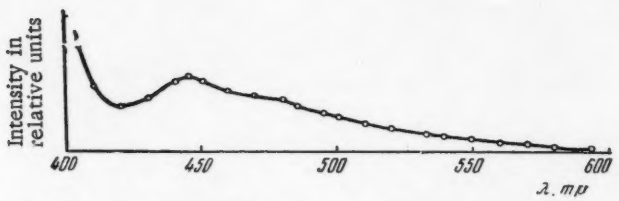


Fig. 4. Luminescence spectrum in the visible range of combined fractions II and III in a solution of heptane (experiment 58).

The physical chemical constants of the remaining isoalkanes were determined, including their solidification temperatures; all of them became glassy masses between 65-75° below zero. In addition their structure was studied by means of infrared spectroscopy, and was found to consist principally of iso forms with tertiary carbon atoms (absorption bands 1170-1140 cm^{-1}). In all these spectra one of the bands was also observed which corresponded to the C–C oscillations of a group containing a quaternary carbon atom. The percentage composition of the hydrocarbons separated and the degree of their conversion are shown in table 4.

On the basis of the results of the study of the composition of the catalytic products of n-nonadecane and eicosane, the following hypothetical scheme for the conversion may be proposed:

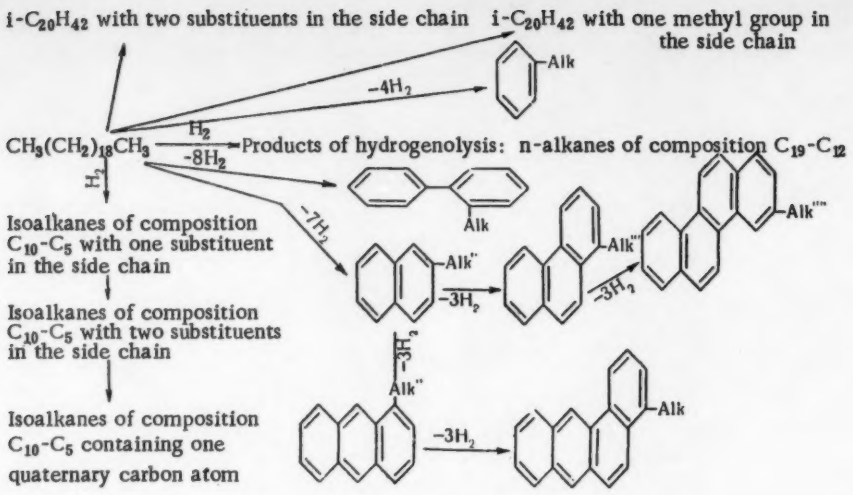


TABLE 3. Chromatographic Analysis of a Mixture of Aromatic Hydrocarbons

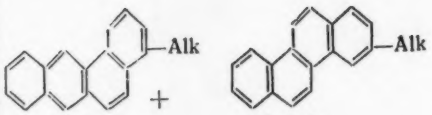
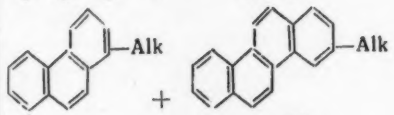
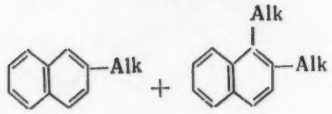
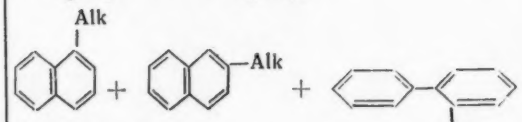
Column with activated Al_2O_3; h = 200 ml	Color of the zone when illuminated by ultraviolet light, λ = 360 mμ	Probable aromatic hydrocarbons
I/	Tarry, non-luminous zone	
II	Zone with green luminescence	
III	Zone with pale blue luminescence	
IV	Zone with blue luminescence	
V	Zone with violet luminescence	
VI	Non-luminescing part	

TABLE 4. Composition of Products Separated from Liquid Products of Catalysis

Hydrocarbon	No. of experiment	Catalyst	Aromatic hydrocarbons, %, by wt.	n-Alkanes with mol. wt. lower than orig. hydrocarbon, % by wt.	Isoalkanes, % by wt.	Cyclanes, % by wt.		Unconverted, % by wt.	% conversion
						5-membered	6-membered		
$n\text{-}C_{19}H_{40}$	51	0.5% Pt–Al_2O_3	7.8	54.7	20.0	1.8	5.1	3.0	97.0
	52	0.5% Pd–Al_2O_3	15.4	41.6	26.6	1.5	5.6	3.5	97.5
	53	0.5% Pt–"gumbrin"	18.4	25.8	49.2	2.0	3.4	1.0	99.0
	54	0.5% Pd–"gumbrin"	27.7	23.7	41.8	2.1	2.6	0.5	99.5

TABLE 4 (continued)

Hydrocarbons	No. of experiment	Catalyst	Aromatic hydrocarbons, % by wt.	n-Alkanes with mol. wt. lower than orig. hydrocarbon, % by wt.	Isoalkanes, % by wt.	Cyclanes, % by wt.		Unconverted, % by wt.	% conversion
						5-membered	6-membered		
$n\text{-}C_{20}H_{42}$	55	0.5% Pt–Al_2O_3	15.4	38.1	20.3	1.9	4.2	2.1	97.9
	56	0.5% Pd–Al_2O_3	13.3	49.3	19.8	2.0	4.1	2.9	97.1
	57	0.5% Pt–"gumbrin"	18.5	20.2	52.3	3.1	6.9	–	100
	58	0.5% Pd–"gumbrin"	22.8	27.3	31.9	2.2	6.0	–	100

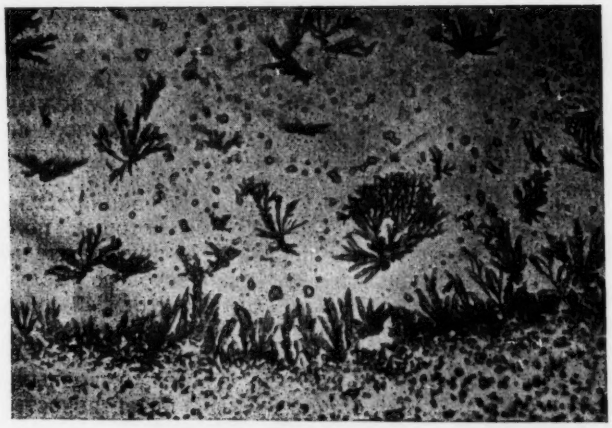


Fig. 5. Crystals separated from the combined fraction II-III after chromatographic separation of the aromatic hydrocarbons on aluminium oxide (contact-catalytic conversion of eicosane).

The optical analysis was done by P. P. Shorygin and Yu. P. Egorov and co-workers, to whom the authors are very grateful. The luminescence spectra were made by A. N. Nikitin, to whom the authors express sincere thanks.

SUMMARY

1. The catalytic conversion of normal nonadecane and of eicosane in the presence of 0.5% Pt–Al_2O_3, 0.5% Pd–Al_2O_3, 0.5% Pt–"gumbrin", and 0.5% Pd–"gumbrin" at 450° in a flow system under a pressure of 30 atm of hydrogen was studied.

2. On catalytic treatment these hydrocarbons undergo profound changes in the direction of isomerization, dehydrocyclization and hydrocracking. The products of catalysis so obtained are characterized by a higher calorific value and a decrease in the temperature of solidification by 20-46°.

3. 0.5% Pt–"gumbrin" and 0.5% Pd–"gumbrin" are more active catalysts in effecting the reactions mentioned than are 0.5% Pt–Al_2O_3 and 0.5% Pd–Al_2O_3.

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THE CATALYTIC ALKYLATION OF TETRALIN

REPORT 3. THE ALKYLATION OF TETRALIN BY NONENE-1 AND N-NONYL ALCOHOL

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pp. 326-329, February, 1961
Original article submitted November 19, 1959

Work on the alkylation of tetralin by nonene-1 and nonanol-1 was undertaken for the purpose of producing monononyltetralin. The synthesis of β-n-nonyltetralin was described by Hart and his co-workers [1]. The authors obtained n-alkyltetralins with alkyl chains varying from C_3 to C_{10} by means of the Friedel-Crafts reaction, with subsequent reduction of the ketones formed. In previous studies we have investigated the alkylation of tetralin by means of amylenes [2] and heptene-1 [3]. The experiments were carried out under pressure in a flow system. Positive results were obtained when the reaction was carried out in contact with aluminium silicate catalysts.

In the present study we investigated the reaction of the alkylation of tetralin by nonene-1 and n-nonyl alcohol at atmospheric and higher pressures in contact with an aluminium silicate catalyst, with zinc chloride on aluminium oxide, and with pure zinc chloride. When the alkylation of tetralin by nonene-1 was carried out in an autoclave in the presence of zinc chloride on aluminium oxide, the yield of β-nonyltetralin amounted to 47.6% calculated on the amount of nonene-1 taken, and 23.3% based on the original tetralin.

The alkylation of tetralin by n-nonyl alcohol went well in the presence of pure zinc chloride. In alkylation experiments in an autoclave at 200°, with a molar ratio of tetralin to nonanol of 2:1, the yield of nonyltetralin was 57% based on the amount of nonyl alcohol used, and was 28.7% based on the tetralin. It was found that the alkylation of tetralin at atmospheric pressure at 180-190° and with a molar ratio of tetralin to n-nonyl alcohol of 1:1 gives a yield of β-nonyltetralin of 50.5% of theoretical calculated on the amount of tetralin used in the reaction; in this case the yield based on the amount of tetralin that actually reacted was ~70%. Thus, the alkylation of tetralin by nonene-1 and nonanol-1 gives satisfactory yields under the conditions that we found. The β-nonyltetralin which is formed gives a sulpha derivative, the sodium salt of which, according to preliminary experiments, appears to be a good detergent.

EXPERIMENTAL

The alkylation of tetralin by nonene-1. The alkylation of tetralin by nonene-1 was carried out at high pressure, in an autoclave and also in a flow system [4]. The nonene-β used for the experiments was obtained by the pyrolysis of n-nonylacetate [5], which had a m. p. of 117° (10 mm); $n^{20}D$ 1.4235, d^{20}_4 0.8642; MR found 54.68; MR calculated for $C_{11}H_{22}O_2$ 54.08. We obtained 368 g of nonylacetate with a yield of 90% of theoretical; its pyrolysis was accomplished by passing it drop by drop at the rate of 20 ml per hour through a tube with an internal diameter of 25 mm which was filled with glass wool and placed in an electric furnace heated to a temperature of 500-510°. The upper layer of the pyrolyzate was separated from the lower acid aqueous layer, washed free from acetic acid, dried, and distilled at atmospheric pressure. 190.0 g of nonene-1 were obtained, 79% of theoretical; it boiled at 147-148° (744 mm) and had $n^{20}D$ 1.4157 and d^{20}_4 0.7286. The following constants are given in the literature [6] for nonene-1: b. p. 146.87°; $n^{20}D$ 1.4157 and d^{20}_4 0.7292. The combination dispersion spectrum that we obtained showed that it was of good purity.

The tetralin used for the reaction had the following properties: b. p. 205-206.5° (752 mm); $n^{20}D$ 1.5425 and d^{20}_4 0.9712. The alkylation of tetralin by nonene-1 in a flow apparatus was done under conditions that we had previously found optimal for this reaction [3], namely at 200°, with a volume velocity of 0.25 per hour under a pressure of 10 atmosphere in contact with an aluminium silicate catalyst. In the reaction we used 66 g (0.5 M) of tetralin and 31.5 g of nonene-1 (0.25 M) or 15.175 g of nonene-1 (0.025). When the molar ratio of tetralin to nonene was 2:1,

the yield of the nonyltetralin fraction with a b. p. of 190-200° (9 mm), $n^{20}D$ 1.5110 was 24.5% based on the nonene-1 and 12.7% based on the tetralin. In the second case, with a molar ratio of tetralin to alkene of 4:1, the yield of this fraction amounted to 50% and 12.7% of theoretical, respectively. The infrared spectra of the fractions obtained corresponded with the spectrum of β-nonyltetralin.

TABLE 1. Alkylation of Tetralin by Nonene-1

Exp. No.	Catalyst	Temperature, °C	Yield of the nonyltetralin fraction with b.p. 190-200° (9 mm).		
			g	% based on nonene-1	% based on tetralin
1	30% $ZnCl_2$ on Al_2O_3	200	25,3	39,2	19,6
2	Same	270	30,5	47,6	23,3
3	Al_2O_3—SiO_2 (85,4%)	270	16,00	24,8	12,4
4	$ZnCl_2$	200	6,0	9,2	4,6
5*	Same	250	44,1	34,1	34,1

* 63 g of nonene-1 used.

TABLE 2. Alkylation of Tetralin by n-Nonyl Alcohol

Exp. No.	Catalyst	Temperature, °C	Molar ratio of tetralin to nonanol	Quantity of catalyst	Nonyltetralin fraction obtained, b.p. 190-200° (9 mm)		
					g	% based on nonyl alcohol	% based on tetralin
6	30% $ZnCl_2$ on Al_2O_3	200	2 : 1	50 ml (45 g)	2,0	31,0	15,5
7	Same	270	2 : 1	45 g	2,8	4,3	2,2
8	Al_2O_3—SiO_2 (85,4%)	270	2 : 1	45 g	19,0	29,4	14,7
9	$ZnCl_2$	200	2 : 1	68,5 g	37,0	57,4	28,7
10	$ZnCl_2$	270	2 : 1	68,5 g	27,2	41,8	26,9
11	$ZnCl_2$	200	1 : 1	68,5 g	49,0	37,9	37,9

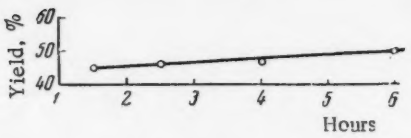
TABLE 3. Alkylation of Tetralin by Nonyl Alcohol at Atmospheric Pressure in the Presence of $ZnCl_2$

Exp. No.	Nonyl alcohol, g	Molar ratio: tetralin to alcohol	Time in hours	Alkyltetralin fract., b.p. 190-200° (9 mm), g	Yield, %	
					based on tetralin	based on nonyl alcohol
12	18,0	4 : 1	5	10,0	7,8	31,4
13	36,0	2 : 1	5	38,5	29,8	60,0
14	72,1	1 : 1	5	65,0	50,5	50,5
15	94,0	2 : 3	5	67,0	51,9	40,0
16	72,1	1 : 1	6	65,5	50,8	50,8
17	72,1	1 : 1	4	60,0	46,5	48,5
18	72,1	1 : 1	2,5	59,0	45,7	45,7
19	72,1	1 : 1	1,5	58,5	45,5	45,5

For the alkylation of tetralin in a rotating autoclave with a volume of one liter we used 66 g (0.5 M) of tetralin and 31.5% (0.25 M) of nonene-1. The experiment was carried out in the presence of 30% $ZnCl_2$ on Al_2O_3 and Al_2O_3-SiO_2 (84.5%) at temperatures of 200, 250 and 270° for a period of five hours. The results obtained are shown in Table 1.

From the data in Table it is evident that zinc chloride on aluminium oxide is an effective catalyst for the alkylation of tetralin by nonene-1; in its presence at 270° the yield of the nonyltetralin fraction amounted to 47.6% of theoretical based on the original tetralin, and to 23.3% calculated on the amount of nonene-1.

The alkylation of tetralin by n-nonyl alcohol. Experiments on the alkylation of tetralin by n-nonyl alcohol were carried out in the presence of the catalysts shown in Table 2, at 200 and 270°, in a rotating autoclave for a period of five hours, and also at ordinary pressure. In each experiment 66 g (0.5 M) were used. The results of the experiments carried out in the autoclave are shown in Table 2.



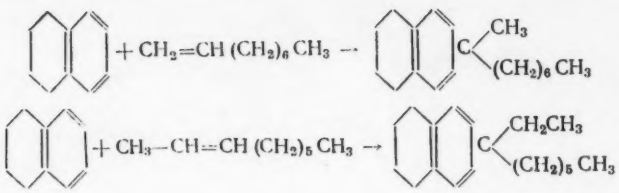
Influence of the length of the reaction on the yield of the nonyltetralin fraction.

From the data in Table 2 it is evident that at 200°, in contact with $ZnCl_2$, the yield of the nonyltetralin fraction reaches 57.4%; increase of the temperature to 270° decreases the yield of the nonyltetralin fraction to 41.8%.

At atmospheric pressure the alkylation of tetralin by nonyl alcohol was carried out in a flask with a mechanical stirrer in the presence of zinc chloride at 185-190°. In each experiment 66 g (0.05 M) of tetralin were used; the quantities of nonyl alcohol are shown in Table 3. Zinc chloride was used in equimolar ratio to the nonyl alcohol. The products of catalysis were distilled in a column with an effectiveness of 15 theoretical plates. This yielded a nonene fraction with a b. p. 144-149 (746 mm). Analysis of it by means of a combination dispersion spectrum showed that it consisted basically of nonene-2 (trans- and cis-isomers) and a small quantity of nonene-1. The tetralin fraction boiled within the limits 200-207° (746 mm); it had $n^{20}D$ 1.5305 and d^{20}_4 0.9630.

The nonyltetralin fraction was separated in a vacuum at 9 mm. It boiled between 190-200° and showed $n^{20}D$ from 1.4900 to 1.5200. Under the conditions that we found to be optimal (experiment 16) the yield of the nonene fraction amounted to 20.5 g, that of the tetralin fraction to 21.0 g, and that of the nonyltetralin fraction to 65.5 g. Based on the amount of tetralin and n-nonyl alcohol used in the reaction, the yield of the nonyl tetralin fraction amounted to 50.8%; calculated on the amounts that actually reacted, it was ~70%. By comparing the influence of the molar ratios of tetralin to nonyl alcohol and the length of the reaction on the yield of alkyltetralins, it was found that an equimolar ratio of the reaction components is optimal (experiments 12-15). Alkylation takes place mainly in the first hour and a half, after which the reaction goes slowly (Fig. 1).

The infrared spectra of the nonyltetralin fractions separated from the products of catalysis in all the experiments on the alkylation of tetralin showed that they were mixtures of β-nonyltetralin with various branchings of the side chain. These branched alkyltetralins apparently are formed not only in the alkylation of tetralin by nonene-1, used in the original reaction mixture, but also by nonene-1 and nonene-2 obtained by the dehydration of n-nonanol in the course of the alkylation reaction since, as was pointed out above, they are found among the products of catalysis.



On the basis of this we believe that in the alkylation of tetralin by nonyl alcohol under the conditions of our experiments, the dehydration of nonyl alcohol first occurs, after which the nonenes formed react to give alkyl derivatives with the tetralin.

The combination dispersion spectrum was taken by G. Gaivoronskaya, and the infrared spectra by V. A. Shlyapochnikov, to whom the authors express sincere thanks.

SUMMARY

Conditions were found for the catalytic alkylation of tetralin by nonene-1 and n-nonyl alcohol with the formation of branched β-nonyltetralins, the yield of which is 47.6% based on the nonene-1 used and 50.5% on the original nonyl alcohol. Calculating on the basis of the amount of tetralin that actually reacted, the yield of β-nonyltetralins amounted to 23.3% and 50.5% respectively.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

MOLECULAR ABSORPTION SPECTRA OF NITROALKANES

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The rapid development of the chemistry of aliphatic nitro compounds raises the problem of finding methods of conveniently and accurately identifying them. Spectroscopic methods of analysis are an important means to this end. In a previous paper we studied the absorption spectra of some gem-dinitrocompounds [1]. The present paper is devoted to the identification of mononitroalkanes, gem-dinitroalkanes and 1,1,1-trinitroalkanes by infrared and ultraviolet spectroscopy.

It is well-known that the $C-NO_2$ group has six normal vibrations and that it gives six absorption bands in the infrared spectrum. Theoretical and experimental study of infrared spectra of the nitroalkanes shows that the absorption band of the antisymmetrical vibrations of the nitro group lies at ~1560 cm^{-1} [2-15] and is very intense. The symmetrical vibration absorption band lies at ~1380 cm^{-1} [2-4, 6-10, 12-14, 16-17] and is somewhat less intense. The C–N vibration absorption band of nitromethane lies at ~920 cm^{-1} [2, 4, 7, 9, 12] and at ~860 cm^{-1} for other mononitroalkanes [3-4, 8, 10, 16-18]. The absorption bands of the deformation vibrations of the nitro group, the out of plane vibrations of the $C-NO_2$ group and the deformation vibrations of C–N–O lie respectively at ~660, 610 and 475 cm^{-1}; they have been studied only in nitromethane, trideuteronitromethane [2, 4, 7, 9, 12], nitroethane, 1-nitropropane and 2-nitropropane [4] – further than this we did not go.

Detailed examination of data in the literature confirms the indication [2, 14] that primary and secondary nitroalkanes may be distinguished from tertiary ones by the absorption bands of the symmetrical and antisymmetrical vibrations of the nitro group, while the primary may be distinguished from the secondary ones by the absorption band of the symmetrical vibration of the nitro group (Table 1).

TABLE 1. Frequencies of the Antisymmetrical and Symmetical Vibrations of the Nitro Group in Primary, Secondary and Tertiary Mononitroalkanes, and also in Gem-dinitroalkanes*

Type of compound	Vibrations of the nitro group, cm^{-1}		Literature references
	antisymmetrical	symmetrical	
$R_1CH_2NO_2$	1554 ± 6	1382 ±6	[2—5],[11—14], [16—18]
$R_1R_2CHNO_2$	1550,5± 2,5	1360,5±3,5	[2—4], [14—15]
$R_1R_2R_3CNO_2$	1538,5± 4,5	1348,5±4,5	[2,14]
$R_1R_4C(NO_2)_2$	1575 ±12	1332 ±5	[1—2], [19—20]

* The data shown are for nitroalkanes in the liquid state or in solution; R_1, R_2 and R_3 are alkyl radicals, while R_4 is either hydrogen or an alkyl radical.

The absorption band of the antisymmetrical vibration of the nitro group lies in a region where there are no other sufficiently intense absorption bands. The situation is somewhat more complicated in the case of the symmetrical vibrations of the nitro group, since the deformation vibrations of the CH_3 group also lie in this region.

Nevertheless superposition of the two bands does not usually occur, and the vibration of the nitro group may be identified by its greater intensity. In addition, the correctness of the assumption may be verified by comparison of the infrared spectrum and the combination dispersion spectrum of the compound in question. Regularities in the change of the absorption band of the C–N vibration were not found [2-4], [7-10], [12, 14]; hence the assignment of this absorption band is complicated since it lies in the region of the C–C skeletal vibrations and has a comparable intensity [2-3]. Consequently this absorption band is inconvenient for the identification of the nitroalkanes. Furthermore, from an analysis of the data in the literature [1-2], [19-20], it appears that in the case of gem-dinitroalkanes that have two such strongly electronegative groups as two nitro groups on one carbon atom, there occurs a shift of the antisymmetrical and symmetrical vibrations of the nitro group to correspondingly higher and lower frequencies, as a result of which it is possible to distinguish the gem-dinitroalkanes from the mononitroalkanes (see Table 1). One may assume, and a single example in the literature (trinitromethane [16]) confirms it, that attaching a third nitro group to the same carbon atom still further increases the displacement of the vibrations of the nitro group.

Thus, examination of the data in the literature on infrared absorption spectra leads us to the conclusion that the fundamental differences in spectra that are suitable for analytical purposes, are to be found in the region of the valence vibrations (1300-1600 cm^{-1}).

In the present study the infrared absorption spectra of the mononitroalkanes and 1,1,1-trinitroalkanes were systematically investigated; the infrared absorption spectra of the gem-dinitroalkanes were published by us previously [1] and are shown for comparison in Table 2. The infrared absorption spectra of the nitroalkanes were taken in the 700-3500 cm^{-1} region on infrared IKS-11 and IKS-12 spectrometers. Study of the compounds was carried out in solutions of tetrachloroethylene, carbon tetrachloride and in the liquid state. Examination of the experimental data shows that the values of the frequency of the vibrations of the mononitroalkanes (Table 3) correspond with the values in the literature [2-6, 11, 14] and are located within the limits indicated in Table 1. Study of the 1,1,1-trinitroalkanes confirmed the assumption in regard to the further displacement of the frequencies of the vibrations of the nitro group; the antisymmetrical vibrations were displaced toward higher, and the symmetrical toward lower frequencies (Table 4).

TABLE 2. Frequencies of the Vibrations of the Nitro Group in Gem-dinitroalkanes in the Liquid State [1]

Formula	Name	Vibrations of the nitro group, cm^{-1}		$\Delta\nu = \nu_a - \nu_c$, cm^{-1}
		antisymmetrical	symmetrical	
$C_2H_4(NO_2)_2$	1,1-Dinitroethane	1582	1331	251
$C_3H_6(NO_2)_2$	1,1-Dinitropropane	1582	1330	252
$C_3H_6(NO_2)_2$	2,2-Dinitropropane	1575	1330	245
$C_4H_8(NO_2)_2$	1,1-Dinitrobutane	1577	1330	247
$(CH_3)_2CHCH(NO_2)_2$	1,1-Dinitro-2-methylpropane	1575	1330	245
$C_5H_{10}(NO_2)_2$	1,1-Dinitropentane	1577	1330	247
$(CH_3)_2CHCH_2CH(NO_2)_2$	4,4-Dinitro-2-methylbutane	1575	1330	247
$C_6H_{12}(NO_2)_2$	1,1-Dinitrohexane	1575	1327	248
$C_7H_{14}(NO_2)_2$	1,1-Dinitroheptane	1577	1330	247
$C_8H_{16}(NO_2)_2$	1,1-Dinitrooctane	1577	1330	247
$C_9H_{18}(NO_2)_2$	1,1-Dinitrononane	1582	1330	252
$C_{10}H_{20}(NO_2)_2$	1,1-Dinitrodecane	1577	1327	250

Thus, clear-cut differences in the infrared absorption spectra of primary, secondary, and tertiary mononitro compounds, gem-dinitroalkanes and trinitroalkanes are observed, which may be utilized for analytical purposes. In addition it is extremely interesting that the difference in the frequencies of the antisymmetrical and symmetrical vibrations ($\Delta\nu = \nu_a - \nu_c$) is also characteristic of the mononitroalkanes, having a value of ~180 cm^{-1}, while the gem-dinitroalkanes have a value of ~250 cm^{-1} and 1,1,1-trinitroalkanes of ~300 cm^{-1}. Consequently this frequency difference may also be used for differentiating mono-, di- and trinitro compounds.

Although this study is primarily concerned with analytical methods, we cannot pass by without mentioning the interesting fact of the reciprocal influence of the nitro group and alkyl radicals. This influence clearly appears in

the infrared absorption spectra of the nitroalkanes and is especially noticeable in the frequencies of the C−H vibrations in the methyl and methylene groups. Assignment of the frequencies of the C−H vibrations was made on the basis of the fact that nitroalkanes with sufficiently long hydrocarbon radicals had frequencies analogous to the frequencies of n-paraffins in the 2800-3100 cm^{-1} region, and these frequencies increased regularly with decreasing length of the radical (Tables 5 and 6 and Figs. 1 and 2). For data on the gem-dinitroalkanes, see [1]. In addition, the correctness of our assignment of the C−H vibrations was confirmed by Linnett's formulas [22]. The change in the angles, calculated by these formulas, is within one degree.

TABLE 3. Frequencies of the Vibrations of the Nitro Group in Mononitroalkanes in the Liquid State

Formula	Name	Vibrations of the nitro group, cm^{-1}		$\Delta\nu=\nu_a-\nu_c$, cm^{-1}
		antisymmetrical	symmetrical	
CH_3NO_2	Nitromethane	1567	1379	188
$C_2H_5NO_2$	Nitroethane	1560	1368	192
n-$C_3H_7NO_2$	1-Nitropropane	1555	1383	172
$(CH_3)_2CHNO_2$	2-Nitropropane	1559	1365	214
n-$C_4H_9NO_2$	1-Nitrobutane	1555	1383	172
$(CH_3)_2CHCH_2NO_2$	1-Nitro-2-methylpropane	1555	1383	172
n-$C_5H_{11}NO_2$	1-Nitropentane	1555	1380	175
$(CH_3)_2CHCH_2CH_2NO_2$	4-Nitro-2-methylbutane	1555	1380	175
n-$C_6H_{11}NO_2$	1-Nitrohexane	1555	1380	175

TABLE 4. Frequencies of the Vibrations of the Nitro Group in 1,1,1-Trinitroalkanes

Formula	Name	Condition	Vibrations of the nitro group, cm^{-1}		$\Delta\nu=\nu_a-\nu_c$, cm^{-1}
			antisymmetrical	symmetrical	
$CH(NO_2)_3$	Trinitromethane	Fusion	1597	1307	290
$C_2H_3(NO_2)_3$	1,1,1-Trinitromethane	Tetrachloroethylene	1603	1298	305
n-$C_3H_5(NO_2)_3$	1,1,1-Trinitropropane	Liquid	1603	1303	300
n-$C_4H_7(NO_2)_3$	1,1,1-Trinitrobutane	"	1603	1305	298
n-$C_5H_9(NO_2)_3$	1,1,1-Trinitropentane	"	1603	1305	298
n-$C_6H_{11}(NO_2)_3$	1,1,1-Trinitrohexane	"	1603	1303	300

Figure 3 shows the dependence of the frequencies of the antisymmetrical C−H vibrations in the methyl group on the length of the alkyl radical for mononitroalkanes, gem-dinitroalkanes (taken from our previously published paper [1] for comparison), and 1,1,1-trinitroalkanes. For the mononitroalkanes this influence is traced up to the fourth carbon atom, for the gem-dinitroalkanes − up to the fifth, and for 1,1,1-trinitroalkanes − up to the sixth.

The influence of the nitro group on the frequencies of the C−H antisymmetrical vibrations in the methyl group may be conceived in a somewhat different manner. Assuming that the length of the C−C bonds in nitroalkanes is not dependent on the length of the radical, it is possible to conceive that the change in frequency $\Delta\nu$ of the C−H antisymmetrical vibration in the methyl group is dependent on the square of the distance r of this group (along the bonds) from the nitro group, thus:

$$\Delta\nu = \frac{A}{r^2}, \qquad (1)$$

where A is a constant. Data on the frequencies of the C−H antisymmetrical vibrations of the methyl group conform to this Eq. (1) within the limits of experimental error.

Formula (1) definitely characterizes the electrostatic interaction of the nitro group and the methyl group and offers an opportunity to evaluate the ratio of the effective action of one, two or three nitro groups in the radical. This ratio is approximately 1:1.5:1.7, i.e., exactly what would be expected from a vector addition of the action of the nitro groups under conditions where the angle between them is tetrahedral. At the present time the measurement of this angle is under study. A more detailed examination of this question would be of considerable interest, but is beyond the limits of this paper.

TABLE 5. C–H Vibrations in Methyl and Methylene Groups in Mononitroalkanes

Formula	Name	C–H vibrations, cm^{-1}			
		CH_3 group		CH_2 group	
		antisymmetrical	symmetrical	antisymmetrical	symmetrical
$CH_3CH_2NO_2$	Nitroethane	3000			
$CH_3CH_2CH_2NO_2$	1-Nitropropane	2981	2884	2945	
$CH_3CH_2CH_2CH_2NO_2$	1-Nitrobutane	2971	2880	2941	
$CH_3CH_2CH_2CH_2CH_2NO_2$	1-Nitropentane	2966	2877	2937	2866
$CH_3CH_2CH_2CH_2CH_2CH_2NO_2$	1-Nitrohexane	2965	2876	2934	2868

TABLE 6. C–H Vibrations of the Methyl and Methylene Groups in 1,1,1-Trinitroalkanes

Formula	Name	C–H vibrations, cm^{-1}			
		CH_3 group		CH_2 group	
		antisymmetrical	symmetrical	antisymmetrical	symmetrical
$CH_3CH_2C(NO_2)_3$	1,1,1-Trinitropropane	2993	2897	2959	
$CH_3CH_2CH_2C(NO_2)_3$	1,1,1-Trinitrobutane	2983	2891	2945	
$CH_3CH_2CH_2CH_2C(NO_2)_3$	1,1,1-trinitropentane	2972	2882	2944	
$CH_3CH_2CH_2CH_2CH_2C(NO_2)_3$	1,1,1-Trinitrohexane	2967	2878	2942	2865
n-Paraffin hydrocarbons [21]		2962	2872	2926	2853

TABLE 7. Ultraviolet Absorption Spectra of the Mononitroalkanes

Formula	Name	Solvent	Maximum		Minimum	
			λ, mμ	ϵ	λ, mμ	ϵ
$n\text{-}C_3H_7NO_2$	1-Nitropropane	Isooctane	279	23.8	247	11.5
		Methylene chloride	277	27.1	–	–
$n\text{-}C_4H_9NO_2$	1-Nitrobutane	Isooctane	279	23.1	246	9.6
		Methylene chloride	279	26.1	–	–
$C_4H_9NO_2$	1-Nitro-2-methylpropane	Isooctane	279	23.0	245	11.0
		Methylene chloride	276	29.7	–	–
$n\text{-}C_5H_{11}NO_2$	1-Nitropentane	Isooctane	279	26.4	247	15.0
		Methylene chloride	277	27.1	–	–
$n\text{-}C_6H_{13}NO_2$	1-Nitrohexane	Isooctane	279	25.2	247	10.1
		Methylene chloride	278	26.7	–	–
		Isooctane	$\epsilon_{cp} = 24.7 \pm 1.7$			

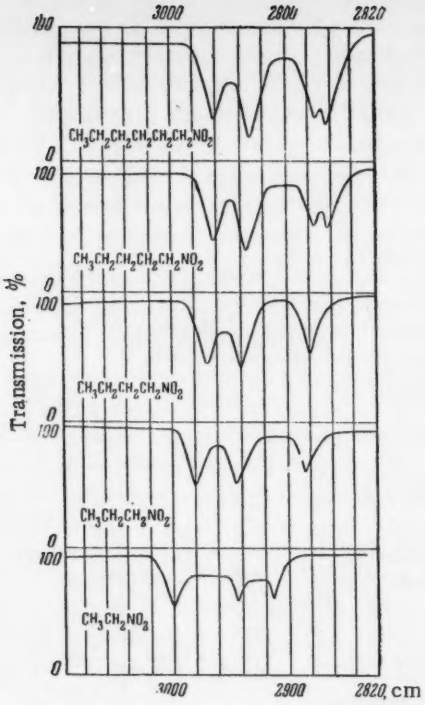

Fig. 1. Infrared absorption spectra of mononitroalkanes in the region of C–H vibrations.

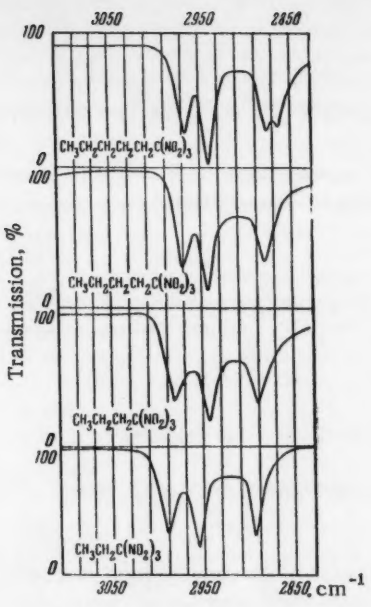

Fig. 2. Infrared absorption spectra of 1,1,1-trinitroalkanes in the region of C–H vibrations.

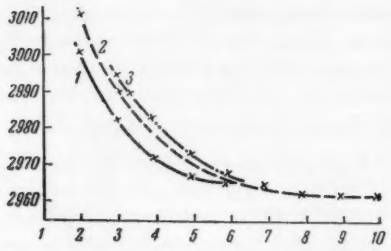

Fig. 3. Dependence of the frequency of the antisymmetrical C–H valence vibrations in the CH_3 group on the length of the alkyl radical: 1) Mononitroalkanes; 2) gem dinitroalkanes; 3) 1,1,1-trinitroalkanes.

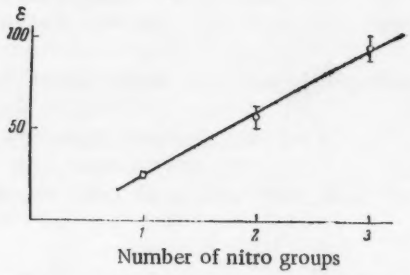

Fig. 4. Dependence of the coefficient of extinction ε when λ = 280 mμ on the number of nitro groups.

The ultraviolet absorption spectra of the mononitroalkanes in the so-called "inactive" nonpolar solvents (heptane, isooctane, petroleum ether) are characterized by a low intensity of electron transition without fine structure at 280 mμ and a high intensity band at 200 mμ [23-26]. In "active" nonpolar and polar solvents (benzene, diozane, carbon tetrachloride, chloroform) the intensity of electron transition at 280 mμ increases, but sometimes a smoothing of the maximum occurs [19]. In reference [26] the limits of the wavelengths of the absorption maxima of primary, secondary and tertiary nitro groups are indicated, but it is not possible to use these differences for analytical purposes since the regions of maximum absorption overlap. Reference [19] indicates that the coefficient of extinction of gem-dinitroalkanes in "inactive" solvents is approximately double that of the mononitroalkanes. The influence of the length of the alkyl radical on the coefficient of extinction is insignificant [3], and the latter has a tendency to increase with increasing length of the radical.

Ultraviolet spectra in our study were obtained on an SF-4 spectrophotometer in solutions of isooctane, n-hexane and methylene chloride. Freshly prepared solutions were used with a concentration of from 2.3-0.6 g/liter; the thickness of the layer was one cm. Data are presented in Tables 7-9.

Figure 4 shows the dependence of the extinction coefficient on the number of nitro groups for solutions in isooctane and n-hexane ($\epsilon = D \cdot MW/c.t$, where D is the optical density; MW is the molecular weight; c is the concentration in g/liter and t is the thickness of the layer). As can be seen from Fig. 4, this is a straight line relationship and consequently it may be used for analytical purposes in determining the number of nitro groups. Since isooctane and n-hexane are not very convenient as solvents because of limited solubility of the polynitroalkanes, we give some examples of the usefulness of methylene chloride as a solvent. The value $\lambda = 280$ mμ is not dependent on the length of the alkyl radical, which is in accord with the data in the literature [3, 26]; moreover it is not dependent on the number of nitro groups.

TABLE 8

Formula	Name	Solvent	Maximum		Minimum	
			λ, mμ	ε	λ, mμ	ε
$C_2H_4(NO_2)_2$	1,1-Dinitroethane	Hexane	281	52	247	21,2
		Methylene chloride	280	53,5	—	—
$C_3H_6(NO_2)_2$	1,1-Dinitropropane	Hexane	281	50,5	247,5	21,0
$C_3H_6(NO_2)_2$	2,2-Dinitropropane	Isooctane	280	60,0	248	27,1
$C_4H_8(NO_2)_2$	1,1-Dinitrobutane	Hexane	280	57,8	247,5	25,0
$C_4H_8(NO_2)_2$	1,1-Dinitro-2-methyl-propane	"	281	63,5	250	29,6
		Methylene chloride	280	65,4	—	—
$C_5H_{10}(NO_2)_2$	1,1-Dinitropentane	Hexane	280	58,2	247,5	22,6
		Methylene chloride	278	61,5	—	—
$C_5H_{10}(NO_2)_2$	4,4-Dinitro-2-methylbutane	Hexane	280	62,0	247,5	28,3
$C_6H_{12}(NO_2)_2$	1,1-Dinitrohexane	"	280	58,1	247,5	20,8
		Methylene chloride	281	67,8	—	—
$C_7H_{14}(NO_2)_2$	1,1-Dinitropentane*	Hexane	281	61,0	247,5	22,4
$C_8H_{16}(NO_2)_2$	1,1-Dinitrooctane*	"	279	60,5	247,0	22,2
$C_9H_{18}(NO_2)_2$	1,1-Dinitrononane*	"	279	60,5	247,0	22,8
$C_{10}H_{20}(NO_2)_2$	1,1-Dinitrodecane*	"	280	64,0	247,5	27,2
		Hexane	$\varepsilon_{cp} = 58 \pm 6$			

*Compounds prepared by V. M. Belikov and L. V. Ershova, to whom the authors express their gratitude.

TABLE 9. Ultraviolet Absorption Spectra of 1,1,1-Trinitroalkanes

Formula	Name	Solvent	Maximum		Minimum	
			λ, mμ	ε	λ, mμ	ε
$C_2H_3(NO_2)_3$	1,1,1-Trinitroethane	Isooctane	278	96,0	260	83,0
		Methylene chloride	279	96,2	—	—
$C_3H_5(NO_2)_3$	1,1,1-Trinitropropane	Isooctane	280	91,0	260	74,1
		Methylene chloride	280	106,0	—	—
$C_4H_7(NO_2)_3$	1,1,1-Trinitrobutane	Isooctane	279	100,0	259	82,0
$C_5H_9(NO_2)_3$	1,1,1-Trinitropentane	"	280	102	258	77,0
$C_6H_{11}(NO_2)_3$	1,1,1-Trinitrohexane	"	279	105,0	259	85,0
		Methylene chloride	280	106,5	—	—
		Isooctane	$\varepsilon_{cp} = 98 \pm 7$			

SUMMARY

1. On the basis of a study of the infrared and ultraviolet absorption spectra of the nitroalkanes and a systematization of the data in the literature, the possibility of identifying mononitroalkanes, gem-dinitroalkanes and 1,1,1-trinitroalkanes by spectroscopic methods was demonstrated.

2. By means of infrared spectroscopy the reciprocal influence of the nitro group and hydrocarbon radicals in nitroalkanes containing one, two or three nitro groups on the end carbon atom was discovered.

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CATALYTIC POLYMERIZATION OF OLEFINS

COMMUNICATION 12. POLYMERIZATION OF ISOBUTYLENE IN THE PRESENCE OF KISATIBI KIESELGUHR

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The polymerizing action of aluminosilicates on olefins was first observed by Gurvich [1] when he treated unsaturated hydrocarbons, from petroleum and also amylene and pinene with weakly calcined natural aluminosilicate-fluoride. The polymerization of isobutylene over aluminosilicates was studied by a number of investigators: Lebedev and co-workers [2] over fluoride, Slobodin [3] over some bleaching clays, Kazanskii and Rozengart [4] over Gayer's synthetic aluminosilicate catalyst. We showed [5] that at 190° and atmospheric pressure isobutylene polymerized in the presence of red clay, whereupon 15-30% of the original olefin changed into a mixture of diisobutylene (about 80%) and triisobutylene. Our object in the current investigation was to determine the catalytic activity of Kisatibi kieselguhr in isobutylene polymerization. Kisatibi kieselguhr served as a carrier for the catalysts in a number of chemical processes: hydrocarbon synthesis from CO and H_2 [6], and hydrogenation and dehydrogenation [7].

EXPERIMENTAL

The apparatus and methods of obtaining isobutylene and carrying out the experiments did not differ from those described earlier [5, 6]. The isobutylene polymerization experiments were carried out at atmospheric pressure by a flow method in a glass reaction tube with internal diameter 10 mm. Kieselguhr (Kisatibi), the composition of which was given earlier [6], served as catalyst. Two forms of the catalyst, both having granule diameter 3 mm, were used; the first was prepared by grinding the rock (100 mesh) followed by molding into granules (catalyst 1), and the second was prepared by direct granulation of the rock (catalyst 2). For comparison a tabletted synthetic aluminosilicate cracking catalyst, the composition of which was given earlier [8], was also studied in the same reaction. The catalysts were not subjected to any treatment prior to the experiments.

Effect of reaction temperature on the yields of isobutylene polymers. A series of experiments was carried out with catalysts 1 and 2 at constant raw isobutylene space velocity ~100 hr^{-1} and with reaction temperatures varying from 110 to 240°. Each experiment was carried out with fresh 30 ml portions of catalyst and lasted ten hours. The results of these experiments, shown in Fig. 1, demonstrated that kieselguhr (Kisatibi) is a very active catalyst for isobutylene polymerization. The yield of liquid polymer, as a percentage of the original isobutylene, was strongly dependent on the reaction temperature and passed through a sharp maximum at 150-160°. The yields of polymers, freed from C_4 hydrocarbons, are given in Fig. 1. The maximum yield amounted to ~75% of the isobutylene passed. Comparable experimental results were obtained with both forms of the catalyst. In the experiments carried out for comparison under similar conditions at temperature 180° with kieselguhr (Kisatibi), synthetic aluminosilicate, and red clay, the polymer yields amounted to 69.6, 81.6, and 30% respectively. Hence, kieselguhr is considerably more active than the clay and its activity is closer to that of the synthetic aluminosilicate; kieselguhr is also a more stable catalyst than the clay: after 40 hr operation, with a break at night, its activity decreased only by 10%, while the clay lost 50% of its original activity in the course of 5-10 hr. It should be noted that in all the experiments shown in Fig. 1, the polymer yields amounted to 90-100% of the isobutylene which had reacted.

Effect of space velocity on the yields of isobutylene polymers. A series of experiments was carried out with samples of catalyst 2 at 160° and raw gas space velocities which were varied from 50 to 650 hr^{-1}. The results are shown in Fig. 2. Increase of space velocity up to 500 hr^{-1} caused the yield of liquid polymer, as a percentage of the isobutylene which was passed, to decrease and the catalyst efficiency to increase. Further increase of space

velocity to 650 hr^{-1} caused both the polymer yield and the catalyst efficiency to decrease. The yield of liquid polymer as a percentage of the isobutylene which had reacted was independent of the raw gas space velocity, remaining at the 96-100% level.

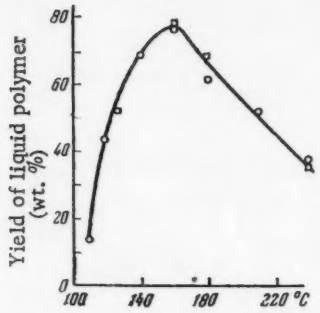

Fig. 1. Yields of liquid polymer, as wt. % of $i\text{-}C_4H_8$ which was passed, in relation to the reaction temperature.

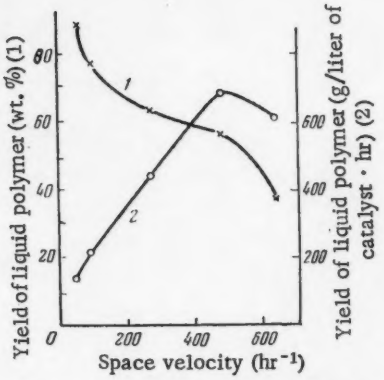

Fig. 2. Yields of liquid polymer in relation to the space velocity of the raw gas: 1) as wt. % of $i\text{-}C_4H_8$ which was passed; 2) in g/liter of catalyst per hr.

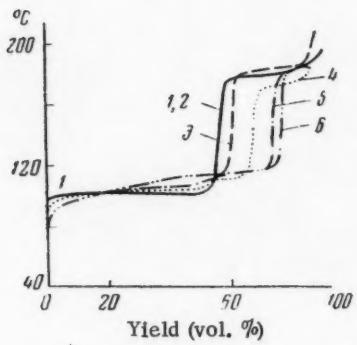

Fig. 3. Distillation curves for polymers produced in the presence of kieselguhr (Kisatibl): 1) at 125°; 2) at 140°; 3) at 160°; 4) at 180°; 5) at 210°; and 6) at 240°.

Effect of reaction conditions on the compositions of the polymerization products. In prolonged experiments at specific temperatures and raw gas space velocities considerable quantities (65-240 ml) of the polymers were accumulated which, after elimination of gases (C_4H_8) by fractionation, were distilled in a column packed with copper pyramids having the effectiveness of 60 theoretical plates. A discrete narrow fraction with boiling point up to 130° was removed. The high-boiling residue was distilled from a Wurtz flask.

Effect of reaction temperature. Isobutylene polymerizations were carried out with constant space velocity of 100 hr^{-1} and temperature varying from 125 to 240°. The results are shown in Tables 1 and 2, and in Fig. 3. As is evident from these data, the polymer obtained at 125° contained practically no products boiling below 101°, i.e., below the boiling point of 2,4,4-trimethylpentene-1 (isobutylene dimer), and above 188°, i.e., above the boiling point of isobutylene trimer, and consisted for the most part only of isobutylene dimers and trimers which were produced in the ratio (by volume) 2:1. The ratio of 2,4,4-trimethylpentene-1 to 2,4,4-trimethylpentene-2 in the dimer fraction amounted to 4:1, and the volume of the remaining isomeric octenes did not exceed 3%. With increase of polymerization temperature the volume of the fraction boiling at 101-102°, corresponding to 2,4,4-trimethylpentene-1, gradually decreased to 14% and the trimer fraction gradually decreased to 8% in the polymer obtained at 240°. A fraction, up to 10%, boiling below 101° simultaneously appeared in the polymer composition, as did a heavy residue which boiled above 188°. Particular interest is aroused by the increase in the isomeric octene fraction, up to 44% in the polymer obtained at 240°, with increase of reaction temperature. It should be noted that the discrete narrow fractions having identical boiling point ranges, shown in Table 2 and also in Table 4, differed little among themselves in the different polymers, as can be seen from their constancy. The fractions boiling at 101-102° had d^{20}_4 0.7149-0.7156 and $n^{20}D$ 1.4087-1.4100, and consisted mainly of 2,4,4-trimethylpentene-1. Literature data [9]: b. p. 101.36°, d^{20}_4 0.7150 and $n^{20}D$ 1.4086. The fraction boiling at 104-105° had d^{20}_4 0.7213-0.7225 and $n^{20}D$ 1.4140-1.4156, and consisted mainly of 2,4,4-trimethylpentene-2. Literature data [9]: b. p. 104.85°, d^{20}_4 0.7212 and $n^{20}D$

1.4160. The constants for the other fractions fluctuated in the following ranges: fractions boiling below 101°: d^{20}_4 0.7011-0.7146 and $n^{20}D$ 1.4066-1.4084; these fractions evidently consisted of olefins with boiling points below those of the C_8 olefins; fractions boiling at 105-130°; d^{20}_4 0.7371-0.7420 and $n^{20}D$ 1.4163-1.4276; fractions boiling at 177-188°: d^{20}_4 0.7595-0.7655 and $n^{20}D$ 1.4315-1.4350; and residues boiling above 188°: d^{20}_4 0.7816-0.7836 and $n^{20}D$ 1.4410-1.4430.

TABLE 1

Polymer properties	Reaction temperature, °C					
	125	140	160	180	210	240
d^{20}_4	0,7207	0,7086	0,7042	0,7088	0,7079	0,7077
n^{20}_D	1,4218	1,4191	1,4188	1,4178	1,4158	1,4185
Boiling commenced (°C)	101	99,5	96	92	94,5	51

TABLE 2

Boiling range of the fraction (°C)	Reaction temperature (°C)					
	125	140	160	180	210	240
	Composition of the fraction (vol. %)*					
< 101	0,0	6,7	4,5	8,9	4,9	10,0
101-102 (2,4,4-trimethyl-pentene-1)	44,4	37,7	36,0	34,8	32,8	14,2
104-105 (2,4,4-trimethyl-pentene-2)	11,4	11,6	13,3	7,9	12,0	9,1
105-130 (isomeric octenes)	2,8	2,6	8,2	12,4	24,4	44,2
177-188 (trimers)	25,5	27,8	23,3	18,5	14,7	7,8
> 188	—	7,0	7,5	5,5	1,3	5,2

* Intermediate fractions are not shown in the table.

TABLE 3

Polymer properties	Isobutylene space velocity (hr^{-1})				
	50	100	500	700	100
	Kieselguhr (Kisatibi)				SAS*
d^{20}_4	0,7172	0,7042	0,7177	0,7055	0,7209
n^{20}_D	1,4205	1,4188	1,4154	1,4148	1,4275
Boiling commenced(°C)	94	96	98,5	101	45

* SAS – synthetic aluminosilicate.

Effect of raw isobutylene space velocity. Isobutylene polymerization reactions were carried out at a constant temperature of 160° and with isobutylene space velocities varying from 50 to 700 hr^{-1}. The results are shown in Tables 3 and 4, and in Fig. 4. The polymers consisted mainly of isobutylene dimers and trimers. With increase of the isobutylene space velocity the 2,4,4-trimethylpentene-1 content increased from 20.5% at space velocity 50 hr^{-1} to 52.5% at space velocity 700 hr^{-1} and the 2,4,4-trimethylpentene-2, isomeric octenes, and, also, trimer contents decreased negligibly. Thus, the yield of high-boiling polymers and isomerization products increased with increase in

TABLE 4

Boiling range of the fraction (°C)	Isobutylene space velocity (hr^{-1})				
	50	100	500	700	100
	Composition of the fraction (vol. %)*				
	Kieselguhr (Kisatibi)				SAS
< 101	17,0	4,5	4,7	0,0	9,8
101-102 (2,4,4-trimethylpentene-1)	20,4	33,4	47,0	52,5	12,4
104-105 (2,4,4-trimethylpentene-2)	10,0	10,6	4,5	7,5	5,6
105-117 (isomeric octenes)	12,4	8,2	5,3	7,3	19,0
177-188 (trimers)	24,0	23,3	18,6	18,4	20,6
> 188	8,0	7,5	1,1	3,1	16,9

* Intermediate fractions are not shown in the table.

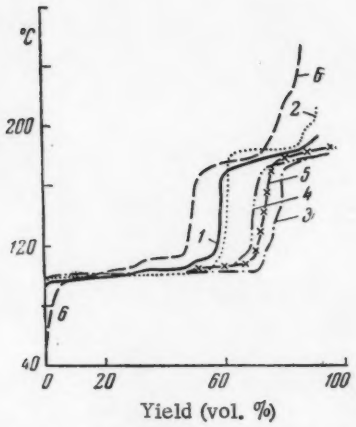

Fig. 4. Distillation curves for polymers produced in the presence of kieselguhr (Kisatibi) with raw isobutylene space velocities of: 1) 50 hr^{-1}; 2) 100 hr^{-1}; 3) 300 hr^{-1}; 4) 500 hr^{-1}; 5) 700 hr^{-1}; and 6) in the presence of synthetic aluminosilicate catalyst.

the contact time. The results of the isobutylene polymerization experiments in the presence of synthetic aluminosilicate cracking catalyst at 160° and space velocity 100 hr^{-1} are shown for comparison in Tables 3 and 4. From these data it is evident that this catalyst promotes the execution of cracking and isomerization processes along with the polymerization reactions. The liquid polymer began to boil at 45° whereas the polymers produced under the same conditions in the presence of kieselguhr began to boil at 96°. In the polymer obtained in the presence of the aluminosilicate the fraction boiling below 101° is double the amount, the fraction of 2,4,4-trimethylpentene-1 is about one-third of the amount, the fraction of 2,4,4-trimethylpentene-2 is one-half of the amount, and the fractions of isomeric octenes and high-boiling residue (b. p. >188°) double the amount of the analogous fractions in a polymer obtained in the presence of kieselguhr.

From the results it is evident that Kisatibi kieselguhr is an active catalyst for isobutylene polymerization, which commences at 100-110° and has an optimum temperature at 150-160°. The reaction products are isobutylene dimers and trimers. The dimer fraction consists mainly of 2,4,4-trimethylpentene-1 and -2. Increase of reaction temperature and decrease of space velocity increase the isomerization both by displacement of the double bond and also, to a certain extent, by cracking. Synthetic aluminosilicate cracking catalyst, having high activity in isobutylene polymerization reactions, possesses a greater degree of cracking and isomerization ability than does kieselguhr.

SUMMARY

1. Kisatibi kieselguhr, which was known earlier only as a carrier for the catalysts in several chemical processes, is a highly active catalyst for isobutylene polymerization.

2. Isobutylene polymerization in the presence of kieselguhr (Kisatibi) occurs at 110-240° (optimum temperature 150-160°) and space velocity 50-700 hr^{-1} (optimum space velocity 500-600 hr^{-1}) with the formation of mainly isobutylene dimers and trimers.

3. Kieselguhr is a more active and stable isobutylene polymerization catalyst than is red clay, and has approximately the same activity as does synthetic aluminosilicate cracking catalyst. However, in the presence of kieselguhr the polymerization is carried out more selectively at the expense of decrease in the proportions of secondary cracking and isomerization reaction products.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SYNTHESIS AND SOME PROPERTIES OF VINYL BORNYL ETHER

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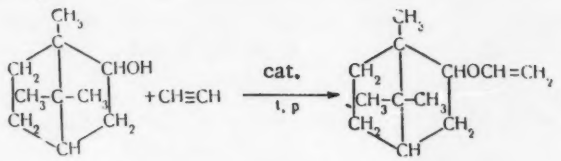
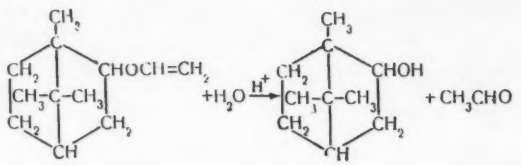
The present communication gives a description of the synthesis and some properties of vinyl bornyl ether, whose conversions have not been studied adequately [1-4]. Of the properties of vinyl bornyl ether, the literature contains only data on the boiling point [2-4] and a report that the compound can form polymeric products [3]. In addition, it was reported that vinyl bornyl ether may be synthesized in butanol in the presence of sodium alcoholate [4].

Vinyl bornyl ether was synthesized by the Favorskii–Shostakovskii reaction [5] under conditions suitable for higher and cyclic alcohols (Eq. 1).

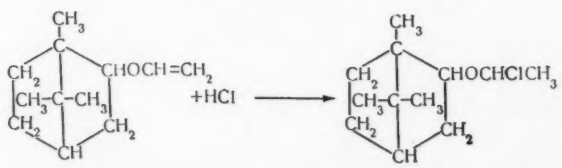


For a successful synthesis it was necessary to use a temperature in the range of 125-180° with a rise toward the end of the experiment and this gave vinyl bornyl ether in 77% yield.

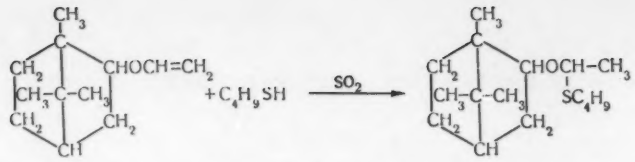
Vinyl bornyl ether is a high-boiling substance, which is stable at the boiling point and has the characteristic odor of the starting alcohol. The chemical properties of vinyl bornyl ether are similar to those of other vinyl ethers, but some reactions require more drastic conditions than other vinyl ethers. For example, vinyl bornyl ether was hydrolyzed by prolonged heating at 100° in the presence of an acid agent (Eq. 2) and this may be explained by the low water-solubility of the borneol formed.



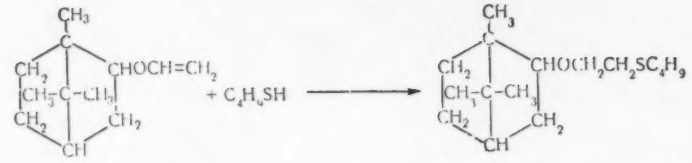
In the presence of traces of hydrogen chloride, vinyl bornyl ether reacted readily with the starting alcohol to form dibornyl acetal, which is a crystalline substance under normal conditions, but may be stored for a long time as a thick mass. Hydrogen chloride added to vinyl bornyl ether to form α-chloroethyl bornyl ether (Eq. 3), a substance which is extremely unstable and turns to tar completely on heating [6].



Under the action of sulfur dioxide, vinyl bornyl ether reacted with butyl mercaptan to give 1-butylmercapto-1-bornyloxyethane in accordance with Markovnikov's rule (Eq. 4).



The latter could be characterized only in the crude form as on distillation, it decomposed completely with the liberation of the starting alcohol. In the presence of azoisobutyronitrile, vinyl bornyl ether added butyl mercaptan largely contrary to Markovnikov's rule (Eq. 5) and partly in accordance with the rule.



1-Butylmercapto-2-bornyloxyethane is a completely stable substance and may be separated from its unstable isomer by heating.

Vinyl bornyl ether polymerized on addition of ferric chloride and boron trifluoride etherate to form friable, pale colored polymers with molecular weights from 1200 to 1400. The yield of the polymer of vinyl bornyl ether in the presence of boron trifluoride etherate was somewhat higher than in experiments with ferric chloride.

Thus, vinyl bornyl ether is quite similar in properties to simple vinyl ethers and in addition, such reaction products as α-chloroethyl bornyl ether and 1-butylmercapto-1-bornyloxyethane are unstable on heating.

EXPERIMENTAL*

Synthesis of vinyl bornyl ether (I). The borneol used for the synthesis was first purified by steam distillation and then its melting point in a sealed capillary was 203-205° and it had $[\alpha]^{20}D = 34.41$ in absolute ethanol [7-9]. A 60-g sample of this borneol was mixed carefully with 6 g of powdered potassium hydroxide (the color of the borneol thereupon changed to cream) and the mixture placed in a 0.8 liter stainless steel rotating autoclave, to which acetylene was then admitted. The autoclave was heated for 2 hr at 125-140° and then for 4 hr at 140-180° until the absorption of acetylene ceased completely. The results of a series of experiments are given in Table 1.

At the end of the experiment, the reaction mixture was diluted with dry ether, filtered to remove the catalyst, and dried with potassium carbonate. After removal of the ether, the residue was distilled twice and its constants were determined: b. p. 69.5-70.5° (4 mm); $n^{20}D$ 1.4730; d^{20}_4 0.9305; $[\alpha]^{20}D$ 101.3. Found MR 54.35; calculated MR 54.39. Found: C 80.10, 79.90; H 11.13, 11.10%. $C_{12}H_{20}O$. Calculated: C 79.94; H 11.18%. Literature data [4]: b. p. 72-74° (2 mm).

TABLE 1. Synthesis of Vinyl Bornyl Ether

Borneol, g	KOH, g	Acetylene in moles per mole of borneol	Heating °C	Heating hr	Acetylene pressure, atm init.	Acetylene pressure, atm final	Yield of vinyl bornyl ether, %	Notes
60	6	1,5	125—140 140—160 160—180	2 2 2	14	4	77,1	10.0 g of resin
51	5,1	1,6	160—180	4	16	6	38,7	20 g of resin + + borneol
30	3,0	2,1	120—140	4	14	11	23,7	Resin + borneol

*G. P. Matveeva helped with the experimental part of the work.

Hydrolysis of vinyl bornyl ether (2). To a sample of vinyl bornyl ether was added 25 ml of 0.5 N hydroxylamine hydrochloride solution and the reaction mixture heated with frequent shaking. After the heating, the hydrochloric acid liberated was titrated with 0.5 N potassium hydroxide solution in the presence of bromophenol blue. The results of hydrolysis experiments are given in Table 2.

TABLE 2. Results of Hydrolyzing Vinyl Bornyl Ether

Sample, g	Heating		ml of 0.5 N KOH	Vinyl bornyl ether found, %
	°C	hr		
0,2584	100	2	2,79	97,40
0,2018	100	2	2,21	98,25
0,8015	20	2	1,88	21,58
0,6178	100	0,5	6,19	90,4
0,8415	100	2	8,96	96,1

In experiments 2-4, the hydrolysis was carried out with 2% sulfuric acid [10] with subsequent addition of hydroxylamine hydrochloride. The experiments at 100° were carried out in sealed ampoules.

Reaction of vinyl bornyl ether with borneol (3). To 18 g (0.1 mole) of vinyl bornyl ether and 7.7 g (0.05 mole) of borneol was added 0.03 g of concentrated hydrochloric acid [11] and then the reaction mixture became homogeneous and the temperature rose to 39°. The mixture was left overnight and then diluted with ether and the catalyst neutralized with potassium carbonate. The ether solution was washed three times with 10% potassium carbonate solution and water, dried with potassium carbonate, and distilled. We obtained an 88% yield of dibornyl acetal with the following constants: b.p. 146-146.2° (1 mm); $n^{20}D$ 1.4846; d^{20}_4 0.9777; $[\alpha]^{20}D$ 80.8. Found MR 97.99; calculated MR 98.28. Found: C 78.71, 78.50; H 11.54, 11.51%. $C_{22}H_{38}O_2$. Calculated: C 78.99; H 11.45%. On prolonged standing, dibornyl acetal crystallized and had m.p. 27-29°.

Hydrochlorination of vinyl bornyl ether (4). A solution of 9.8 g of vinyl bornyl ether in diethyl ether was cooled to −20° and a stream of dry hydrogen chloride passed in at such a rate that the temperature of the reaction mixture did not rise above −5°. After the removal of the excess hydrogen chloride and diethyl ether in vacuum, the reaction mixture consisted of a pale yellow liquid. When heated in vacuum in a stream of dry nitrogen, it resinified completely with partial liberation of borneol.

The experiment was repeated under the above conditions, but the reaction mixture was used for hydrolysis immediately after removal of the excess hydrogen chloride and diethyl ether. After the substance had been shaken vigorously with water for several minutes, the hydrochloric acid in the hydrolyzate was determined by alkalimetry and the acetaldehyde by oxime formation. The hydrochloric acid content of the hydrolyzate was 70.1% and the acetaldehyde content 69-70%.

Addition of butyl mercaptan to vinyl bornyl ether in the presence of sulfur dioxide (4). A mixture of 3 g of butyl mercaptan and 6.4 g of vinyl bornyl ether, that had been distilled in a stream of dry nitrogen, was cooled to −20° and a stream of dry sulfur dioxide passed through the mixture for 30 sec [12]. The temperature of the reaction mixture thereupon rose to 30° and was then kept at 20° for 2 hr. The mixture was diluted with ether, washed five times with 10% sodium hydroxide solution and with water, and dried with sodium sulfate. The mixture was distilled in a stream of dry nitrogen. We obtained: fraction I with b. p. 68-105° (3 mm); $n^{20}D$ 1.4730; 1.5 g. Fraction II with b. p. 105-125° (3 mm); $n^{20}D$ 1.4808; 0.5 g. Fraction III with b. p. 125-130° (3 mm); $n^{20}D$ 1.4848; 5.9 g.

With a 20% alcohol solution of mercuric chloride, fractions II and III gave voluminous precipitates, which became red in the presence of Methyl orange [12]; at the same time, the first and second fractions contained borneol. When fraction III was cooled to −20°, it deposited crystals of borneol, which were separated from the liquid part by decantation and according to titration data, the latter contained 95-98% of 1-butylmercapto-1-bornyloxyethane.

Under the conditions of the previous experiment we isolated a product which was characterized in the crude form after removal of the diethyl ether. The content of 1-butylmercapto-1-bornyloxyethane was 95.24-95.0%. The physical constants were as follows: d^{20}_4 0.9459; $n^{20}D$ 1.4830; $[\alpha]^{20}D$ 70.83. Found MR 81.67; calculated MR 81.30. Found: C 70.74, 70.72; H 11.10, 11.21; S 11.60, 11.51%. $C_{16}H_{30}OS$. Calculated: C 71.03; H 11.18; S 11.85%.

Addition of butyl mercaptan to vinyl bornyl ether contrary to Markovnikov's rule (5). To effect the addition under the influence of traces of oxygen, we heated 4.5 g of butyl mercaptan and 10 g of vinyl bornyl ether in a sealed ampoule at 100° for 24 hr [12]. The reaction mixture was diluted with diethyl ether, washed three times with 10% sodium hydroxide solution and with water, and dried with sodium sulfate. The diethyl ether was removed in vacuum and the residue distilled in a stream of dry nitrogen. We obtained: fraction I with b. p. 75° (6 mm); $n^{20}D$ 1.4733; 0.8 g. Fraction II with b.p. 75-153° (6 mm); $n^{20}D$ 1.4811; 0.6 g. Fraction III with b.p. 153-162° (6 mm); $n^{20}D$ 1.4877; 11.6 g.

The yield of addition products was 86.6%. Fraction I was vinyl bornyl ether and fraction III was the product from addition of the mercaptan contrary to Markovnikov's rule with some 1-butylmercapto-1-bornyloxyethane. The main reaction product was freed from its isomer by heating to 180° (20 mm) in a nitrogen atmosphere and after redistillation, it had the following constants: b. p. 159-161° (5 mm); $n^{20}D$ 1.4886; d^{20}_4 0.9604; $[\alpha]^{20}D$ 51.27. Found MR 81.26; calculated MR 81.22. Found: C 70.95, 70.85; H 11.29, 11.27; S 11.81, 11.99%. $C_{16}H_{30}OS$. Calculated: C 71.03; H 11.18; S 11.85%. The product isolated was 1-butylmercapto-2-bornyloxyethane.

For studying the reaction of butyl mercaptan with vinyl bornyl ether in the presence of azoisobutyronitrile, we heated a mixture 3.6 g (0.045 mole) of butyl mercaptan, 16 g (0.09 mole) of vinyl bornyl ether, and 0.08 g of azoisobutyronitrile in an ampoule in dry nitrogen at 60° for 6 hr and distilled the product [13]. The addition product (9.4 g, 87%) was a mixture of 1-butylmercapto-2-bornyloxyethane and 1-butylmercapto-1-bornyloxyethane with 7.7-7.8% of the latter according to titration [12].

Polymerization of vinyl bornyl ether. For polymerization in the presence of ferric chloride, one drop (0.01 g) of ferric chloride solution was added to 4.8 g of freshly distilled vinyl bornyl ether in the cold and the mixture heated to 225° [14]. When this temperature was reached, a further 2 drops of catalyst were added and the mixture heated at 220-225° for 1.5 hr. The cooled reaction mixture was brown and vitreous and was precipitated twice from dry benzene with methanol. The powder obtained was soluble in diethyl ether and carbon tetrachloride and insoluble in methanol, ethanol, and acetone. The characteristics of the polymer are given in Table 3.

TABLE 3. Characteristics of Polymers of Vinyl Bornyl Ether

Mol. wt.	M.p. °C	Catalyst	Elementary analysis, found, %		Elementary analysis, calc., %		Polymer yield, %
			C	H	C	H	
1326	165—167	Ferric chloride	80,00 80,00	11,15 11,20	79,94	11,18	46,6
1174	154—156	Boron trifluoride etherate	79,79 79,54	10,99 11,29	79,94	11,18	89,6

No polymer was formed under the above conditions if all the catalyst was introduced at once and not in portions.

For polymerization in the presence of boron trifluoride etherate, 3 drops of a 5% solution of boron trifluoride etherate (0.03 g) were added to 5 g of vinyl bornyl ether [15], whereupon the temperature rose to 110° and the reaction mixture changed to a viscous, pale brown polymer. The polymer obtained was precipitated twice from dry diethyl ether with methanol. The properties of the polymer are given in Table 3.

SUMMARY

1. Vinyl bornyl ether was synthesized and some of its conversions were studied.
2. Vinyl bornyl ether readily forms an acetal with the starting alcohol and also adds hydrogen chloride.
3. Butyl mercaptan react with vinyl bornyl ether either according to or contrary to Markovnikov's rule.
4. Vinyl bornyl ether undergoes polymerization to given polymers with molecular weights of 1200-1400.

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SOME CONVERSIONS OF VINYL MENTHYL ETHER

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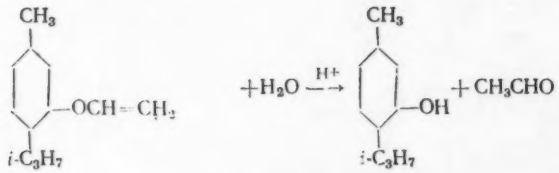
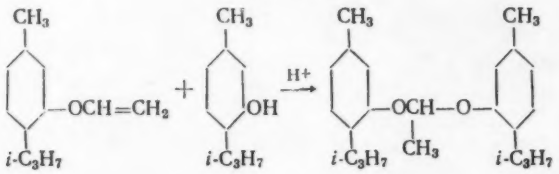
Original article submitted August 24, 1959

The synthesis of vinyl menthyl ether has been described in the literature [1-4], but data on its reactivity are very limited. We prepared vinyl menthyl ether by the Favorskii-Shostakovskii reaction [5]. A study of the reactivity of vinyl menthyl ether showed that the compound is similar to vinyl cyclohexyl ether in a number of reactions, but also has its own peculiarities. For example, while vinyl cyclohexyl ether was hydrolyzed completely at room temperature by 2% sulfuric acid in 30 min [6], only 17% of vinyl menthyl ether was hydrolyzed at the same temperature in 2 hr. Vinyl menthyl ether could be hydrolyzed completely in an acid medium in 2 hr at 100° (Eq. 1).



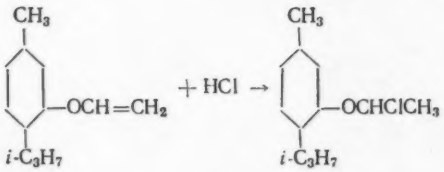
(1)

At the same time, vinyl menthyl ether reacted readily with menthol in the presence of catalytic amounts of concentrated hydrochloric acid to form dimenthyl acetal (Eq. 2) [6].



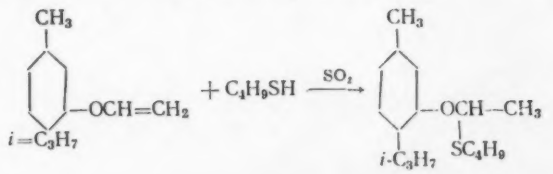
(2)

Vinyl menthyl ether added dry hydrogen chloride (Eq. 3), but the α-chloroethyl menthyl ether obtained was unstable and resinified completely on heating, while α-chloroethyl cyclohexyl ether distills readily in a stream of nitrogen without decomposition [6].



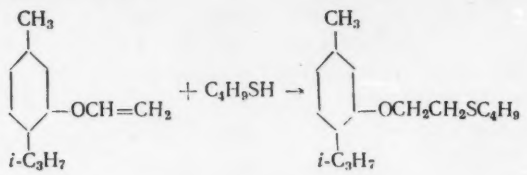
(3)

Butyl mercaptan reacted with vinyl menthyl ether in the presence of sulfur dioxide to form 1-butylmercapto-1-menthyloxyethane (Eq. 4) [7], which, however, could not be isolated in a pure form as it decomposed completely on heating with the liberation of menthol, crude dibutyl mercaptal, and resin.



(4)

When kept for a long time in air or when heated in a sealed ampoule at 60°, vinyl menthyl ether and butyl mercaptan formed a mixture of addition products, contrary to Markovnikov's rule (Eq. 5), with a small amount of the addition product in accordance with the rule.



(5)

It is reported in the literature that hydrogen sulfide reacts with vinyl cyclohexyl ether [8] to form a mixture of products of normal and iso structure.

Vinyl menthyl ether polymerized in the presence of ferric chloride and boron trifluoride etherate to form friable solid polymers with molecular weights of 1200-1300 [9, 10], i.e., it behaved similarly to vinyl cyclohexyl ether in this process [11]. We were unable to polymerize vinyl menthyl ether by means of azoisobutyronitrile, though this polymerization has been described for vinyl cyclohexyl ether [11].

Thus, the presence of alkyl radicals in the ring of vinyl menthyl ether increases the instability of its derivatives in comparison with derivatives of vinyl cyclohexyl ether.

EXPERIMENTAL*

Synthesis of vinyl menthyl ether. For the preparation of vinyl menthyl ether we used menthol with m. p. 39-40° and $[\alpha]^{20}D$ 50.47 in absolute ethanol [12]. The synthesis was carried out under the conditions described previously [3].

The vinyl menthyl ether was obtained in 73.5% yield and after treatment with sodium; it had the following constants: b. p. 69-70° (3 mm); b. p. 212.5-213.5° (corr.); $n^{20}D$ 1.4550; d^{20}_4 0.8586; $[\alpha]^{20}D$ 73.69; found MR 56.94; calculated MR 56.59. Found: C 79.00, 79.00; H 12.20, 12.30%. $C_{12}H_{22}O$. Calculated: C 79.05; H 12.16%. Literature data [1]: b. p. 95-96° (17 mm) and [3]: b. p. 70-72° (2 mm); $n^{20}D$ 1.4580; d^{20}_4 0.8727.

Hydrolysis of vinyl menthyl ether (1). The results and experimental conditions are given in Table 1. The acetaldehyde formed during hydrolysis of the ether with 2% sulfuric acid was determined by oxime formation [13].

TABLE 1. Results of Hydrolysis of Vinyl Menthyl Ether

Exp. No.	Sample, g	Heating temperature, °C	Heating time, hr	ml of 0.5 N KOH	Vinyl methyl ether found, %
1*	0,1424	100	2	1,55	99,11
	0,1581	100	2	1,72	98,57
2	0,7009	20	2	1,26	16,43
3	0,8423	100	0,5	8,75	88,24
4	0,8260	100	2	8,90	98,28

*The hydrolyzing agent was hydroxylamine hydrochloride solution in experiment 1 and 2% sulfuric acid in experiments 2-4. The experiments at 100° were carried out in ampoules.

Reaction of vinyl menthyl ether with menthol (2). To 7.8 g of menthol (0.05 mole) and 18.2 g (0.1 mole) of vinyl menthyl ether was added 0.03 g of concentrated hydrochloric acid [14], when the temperature rose to 45°. The mixture was left overnight and then diluted with diethyl ether and washed with potassium carbonate solution and water. Drying with potassium carbonate and distillation gave an 89.9% yield of a substance with the following constants:

*G. P. Matveeva helped with the experimental part of the work.

b. p. 174-176° (5 mm); $n^{20}D$ 1.4646; d^{20}_4 0.9096; $[\alpha]^{20}D$ 117.9; found MR 102.8; calculated MR 102.68. Found: C 77.80, 77.70; H 12.51, 12.60%. $C_{22}H_{42}O_2$. Calculated: C 78.04; H 12.50%. The substance was dimenthyl acetal.

Hydrochlorination of vinyl menthyl ether (3). A stream of dry hydrogen chloride was passed through 9.1 g of vinyl menthyl ether [6] at −20°. When the increase in weight reached ~2 g, the reaction was stopped. The excess hydrogen chloride was removed in a stream of dry nitrogen under reduced pressure. The substance had a pale yellow color. The hydrochloric acid content of the hydrolyzate equalled 76.2% and the acetaldehyde content was 77.6%, as determined by oxime formation. There was decomposition with the formation of menthol and resin during vacuum distillation of the reaction product.

Addition of butyl mercaptan to vinyl menthyl ether (4 and 5). For addition according to Markovnikov's rule, a mixture of 5.2 g of freshly distilled butyl mercaptan and 10.4 g of vinyl menthyl ether was cooled to −20° and a stream of dry sulfur dioxide passed through the mixture for 30 sec [7]. The temperature rose to 30° and was then kept at 20° for 2 hr. The mixture was left overnight, neutralized with powdered potassium carbonate, filtered, and distilled: fraction I had b. p. 84-100° (4 mm); $n^{20}D$ 1.4710; 10.3 g; fraction II had b. p. 100-152° (4 mm); $n^{20}D$ 1.4840; 3.1 g. Menthol separated when fraction I was cooled. The addition of an alcohol solution of mercuric chloride to fraction II and subsequent titration with alkali [7] showed that it contained 87.5% of dibutyl mercaptal.

For addition contrary to Markovnikov's rule, 4 g of butyl mercaptan and 9.3 g of vinyl menthyl ether were heated in an ampoule at 100° for 24 hr. The contents of the ampoule were diluted with diethyl ether, washed with 10% sodium hydroxide solution and water, and dried with sodium sulfate. Distillation yielded the following fractions: fraction I with b. p. 95° (10 mm); $n^{20}D$ 1.4580; 1.0 g; fraction II with b. p. 95-170° (10 mm); $n^{20}D$ 1.4712; 0.8 g, and fraction III with b. p. 170-175° (10 mm); $n^{20}D$ 1.4762; 9.6 g.

Fraction I was vinyl menthyl ether, while fraction II gave an acid reaction with an alcohol solution of mercuric chloride in the presence of methyl orange, indicating the presence of 1-butylmercapto-1-menthyloxyethane. Fraction III had a neutral reaction when treated with an alcohol solution of mercuric chloride in the presence of methyl orange and after redistillation, it had the following constants: b. p. 163-165° (6 mm); $n^{20}D$ 1.4762; d^{20}_4 0.9209; $[\alpha]^{20}D$ 66.23; found MR 83.47; calculated MR 83.50. Found: C 70.49, 70.52; H 11.50, 11.84; S 11.69, 11.76%. $C_{16}H_{32}OS$. Calculated: C 70.52; H 11.84; S 11.76%. The product obtained was 1-butylmercapto-2-menthyloxyethane.

Polymerization of vinyl menthyl ether. We studied the polymerization of vinyl menthyl ether under the action of ferric chloride solution and boron trifluoride etherate under the conditions described for vinyl bornyl ether [15]. The polymers obtained were purified by solution in diethyl ether and subsequent precipitation with methanol. The polymers of vinyl menthyl ether were pale solids, which were soluble in diethyl ether, benzene, and carbon tetrachloride and insoluble in ethanol, methanol, and acetone. The characteristics of the polymers are given in Table 2.

TABLE 2. Characteristics of Polymers of Vinyl Menthyl Ether

Expt. No.	Catalyst	Mol. wt.	M. p., °C	Elementary composition, %				Polymer yield, %
				found		calculated		
				C	H	C	H	
1	Ferric chloride	1238.0	112-114	78.79 78.55	12.10 12.00	79.05	12.16	56.25
2	Boron trifluoride etherate	1260.0	95-97	78.81 78.84	11.96 11.89	79.05	12.16	57.6

SUMMARY

1. The reactions of vinyl menthyl ether with water, hydrogen chloride, and butyl mercaptan and also the polymerization of the ether were studied.

2. Vinyl menthyl ether is a very reactive substance, but some of its addition products are thermally unstable.

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AN INVESTIGATION IN THE FIELD OF CHEMICAL CHANGES OF UNSATURATED AND HIGH-MOLECULAR COMPOUNDS

COMMUNICATION 16. COPOLYMERIZATION OF VINYL ETHERS AND VINYL ESTERS

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Original article submitted December 4, 1959

As a result of investigations in the field of copolymerization, carried out during the last decade, a theory was developed which accounted for the reactivity of a number of monomers during copolymerization. With the aid of composition equations, which were evolved in differential and integral form, it is possible to evaluate the relative activities of the monomer radicals participating in the copolymerization (r_1 and r_2) [1]. Conclusions concerning possible cases of copolymerization can be drawn on the basis of the concept of the constants r_1 and r_2 and analysis of these equations [2]. Among these cases are those which have for the two copolymerizating monomers a constant value of (r_1 or r_2) equal to zero. Such monomers are believed to be compounds which are unable to polymerize alone [3], for example, 1,2-disubstituted ethylenes and vinyl ethers. For the latter the relative activity of the radical (r_2) starts equal to zero during copolymerizations with vinyl acetate, styrene, and acrylonitrile [1], i.e., vinyl ethers, in accordance with the above stated concepts, cannot form polymeric chains. In fact for some time attempts to initiate polymerization of vinyl ethers alone by the radical mechanism failed [4]. In recent years Shostakovskii and Gladyshevskaya have shown that vinyl ethers polymerize alone by the radical mechanism in the presence of dinitrile azoisobutyric acid (Table 1) [5].

On the basis of these experimental data it is necessary to define more exactly the concept of the reactivity of vinyl ethers during copolymerization. It is evidently also necessary to ascertain the utility of the differential and integral composition equations for assessment of the reactivity of vinyl ethers during copolymerization. With this object the constants (r_2) were calculated for vinyl ethers during their copolymerization with vinyl esters. In order to calculate the relative reactivities of the radicals (r_2) we used experimental data obtained in the case of copolymerization of methylmethacrylate (r_1) and vinylbutyl ether (r_2), when the following constants were determined: $r_1 = 1.6 \pm 0.2$ and $r_2 = 0.2 \pm 0.1$ [6]. The constant (r_2) for vinylethyl ether during its reaction with vinylacetate is also negative according to Mayo's data [7]. A similar situation was observed in the case of copolymerization of chloroprene (r_1) and vinyl formate (r_2), $r_1 = 15.0$ and $r_2 = -0.035$ [8], i.e., the differential and integral equation cannot be used to calculate the copolymerization constants for those cases when the differences between the starting concentrations of the monomers and the amounts of them which do not enter into reaction are small. A negative value of the copolymerization constant, as is known, is useless for assessment of the monomer reactivity during copolymerization. In these cases it is useful to adjust the value (r_2) to zero when the monomers in fact do not polymerize alone. Vinyl ethers, as is shown above, are able to add to their own radicals in the case of polymerization by the radical mechanism. Hence it was to be expected that this property of vinyl ethers would survive during copolymerization, and copolymers with the number of vinyl ether units greater than 50 mol. % will be formed. There is a great deal of data in the literature concerning the entry of less than 50 mol. % of vinyl ethers into copolymers. These data were obtained at specific copolymerization constants, i.e., with copolymer yields less than 20%.

We studied the copolymerization of vinyl ethers and acrylic acid derivatives with maximum transformation of the raw monomers. In all experiments the copolymers which were obtained contained not more than 50 mol. % vinyl ether units. It was desirable to supplement these data with new experiments which were carried out at different temperatures in the presence of atmospheric oxygen with benzoyl peroxide and dinitrile azoisobutyric acid initiators. The experimental results are given in Table 2 in which are shown the dependences of yields and compositions of methylmethacrylate and vinylbutyl ether copolymers on reaction temperature and initiator.

From the data in Table 2, it is evident that the nature of the initiator influences the copolymerization reaction; in the presence of dinitrile azoisobutyric acid the number of vinyl ether units in the copolymer increases, but does not exceed 50 mole %. Increase in reaction temperature decreases the yield and the number of vinyl ether units in the copolymer. The results of copolymerizations in atmospheres of nitrogen and air are shown in Table 3.

TABLE 1. Yields and Mole Wt. of Vinylalkyl Ethers in the Case of Polymerization by the Radical Mechanism

Polymerization temp.,°C	Duration of experiment (hrs)	Amount of dinitrile azoisobutyric acid (%)	Polymer yield (%)	Mol. wt. of polymer
60*	130	0,1	6,8	4120
60*	130	0,5	16,4	3670
60*	130	1,0	22,2	3400
60**	130	0,1	7,2	3075
60**	130	0,5	22,0	2600
60**	130	1,0	25,0	2400

* For polyvinylethyl ether.
** For polyvinylbutyl ether.

TABLE 2. Influence of Initiators and Temperature on Yields and Compositions of Vinylbutyl Ether (II) and Methylmethacrylate (I) Copolymers

Molecular composition of raw monomers (%)		Yield (%)	Molecular composition of the units in the copolymer (%)		Amounts of monomers not entering into the copolymer (%)		Remarks
I	II		I	II	I	II	
25	75	32.3	74.0	26.0	4.5	88.9	Initiator Bz_2O_2, polymerization temp. 60 ± 1°
25	75	30.5	63.75	36.25	22.3	85.0	Initiator dinitrile azoisobutyric acid, polymerization temp. 60 ± 1°
25	75	20.0	78.33	21.67	36.9	94.2	Initiator dinitrile azoisobutyric acid, polymerization temp. 90 ± 1°

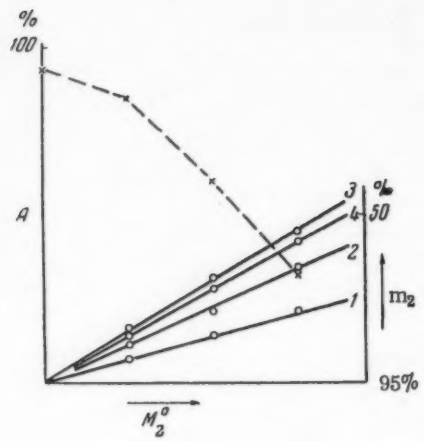
Hence, it follows that vinyl ethers, although they polymerize alone by the radical mechanism, do not add onto their own radicals during copolymerization, i.e., they act as in the case of heteropolymerization [3]. Therefore, the allegation of Ushakov and his co-workers [3] that monomers which do not add to their own radicals during copolymerization are unable to polymerize alone is inapplicable in the stated case. Meanwhile, a knowledge if only of the relative rates of addition of the monomers to "foreign" radicals is of considerable interest for assessment of the reactivity of vinyl ethers and other vinyl compounds. It is particularly necessary for vinyl ether radicals since there is no method of determining the relative or absolute rates of addition to them of "foreign" monomers.

In connection with this we attempted to find a method by which it would be possible to compare the relative rates of addition of monomers to foreign radicals. It is possible to develop such a method, for example, if conditions can be established under which copolymerization proceeds only by addition of the monomers to "foreign" radicals, and addition of the monomers to "their own" radicals is excluded. In connection with this, experimental data which was obtained from vinyl ether and vinyl ester copolymerizations [9] was manipulated. As a result of this a

simple relationship between the starting concentrations of the vinyl ethers in the reaction medium and the number of vinyl ether units in the copolymer was established (Fig. 1). This relationship is described by the straight-line equation

$$m_2 = KM_2, \quad (1)$$

where m_2 is the number of vinyl ether units in the copolymer in mole %, M_2 is the starting concentration of vinyl ethers in the reaction medium in mole %, K is a proportionality coefficient, corresponding to tgα, and α is the angle between the axis of abscissas and the straight line corresponding to the copolymer compositions.

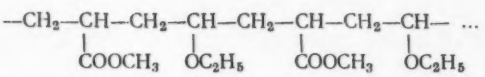


Relationship between vinyl ether concentration and number of vinyl ether units in copolymers: m_2 is mole % content of vinyl ether units, M_2^0 is starting concentration of vinyl ether, A is % yield, and x refers to A. 1) Methylmethacrylate and vinylethyl ether copolymer; 2) methylmethacrylate and vinylphenyl ether copolymer; 3) methylacrylate and vinylethyl ether copolymer; 4) methylacrylate and vinylphenyl ether copolymer.

For Eq. (1) the following quantities are established experimentally: M_2 – the vinyl ether concentration (mole %) which is assigned for the copolymerization with the vinyl ester; m_2 – the number of vinyl ether units in the copolymer (mole %) which is found from the experimental data.

The constant K is determined from two or more vinyl ether and vinyl ester copolymerization experiments carried out with different monomer molar ratios. In our investigations the quantitative relationship between the concentration of vinyl ether in the reaction medium and the number of vinyl ether units in the copolymer was determined from the data obtained from three copolymerization experiments carried out with different raw monomer ratios. The K values for several vinyl ethers are given in Table 4.

The constants (K) characterize the activities of vinyl ethers during their copolymerizations with methyl esters of acrylic and methacrylic acids; the greater is K, the more active is the vinyl ether during copolymerization. Knowing constant K, the copolymer composition can be calculated with the aid of Eq. (1). Constant K together with Eq. (1) enables the starting concentration of vinyl ether with which the number of its units in the copolymer attains 50 mole % to be calculated. For example, from the data in Table 4 it can be calculated that methylmethacrylate and vinyl ethers do not form copolymers containing 50 mole % vinyl ether units at any raw monomer molar ratio. This was confirmed experimentally [9]. The starting monomer concentrations for the production of copolymers with regularly alternating units can be determined for methylacrylate and vinyl ethers. As an example, we calculated the starting concentrations of methylacrylate and vinylethyl ether with which the copolymer will have a regular alternation of the units. From the data in Table 4 and Eq. (1) we found the concentrations at which the copolymer will have the structure [9]



and contain 50 mole % of the units of each monomer: $m_2 = KM_2$; m_2 = 50 mole %, K = 0.55, M_2 = 90.9 mole %; i.e., vinylethyl ether requires to be 90.9 mole % and methyl acrylate requires to be 9.1 mole % of the raw mixture. With the given raw monomer concentrations regular alternation of the units of each of the monomers is possible with absence of addition of these monomers to "their own" radicals. In this case the reaction can be represented by the following scheme:

$$m_1^{\cdot} + M_2 \xrightarrow{K_2} m_1M_2^{\cdot}, \quad (2)$$

$$m_2^{\cdot} + M_1 \xrightarrow{K_4} m_2M_1^{\cdot}, \quad (3)$$

where m_1^* is the vinyl ester radical, m_2^* is the vinyl ether radical, M_1 is the vinyl ester starting concentration, M_2 is the vinyl ether starting concentration, K_2 is the rate constant for the addition reaction M_2 to m_1^*, and K_4 is the rate constant for the addition reaction M_1 to m_2^*.

TABLE 3. Yields and Compositions of Vinylbutyl Ether (II) and Methylmethacrylate (I) Copolymers

Molecular composition of raw monomers (%)		Yield, (%)	Molecular composition of the units in the copolymer (%)		Amounts of monomers not entering into the copolymer (%)		Remarks
I	II		I	II	I	II	
50	50	53.72	83.66	16.34	10.65	82.4	In an atmosphere of air
50	50	53.95	87.5	12.5	5.5	86.4	In an atmosphere of nitrogen

TABLE 4. Values of K for Several Vinyl Ether and Vinyl Ester Copolymers

I	II	K for molecular ratios			
		I / II	75% / 25%	50% / 50%	25% / 75%	average value
$CH_2=C(CH_3)COOCH_3$	$CH_2=CHOC_2H_5$		0,26	0,29	0,29	0,28
$CH_2=C(CH_3)COOCH_3$	$CH_2=CHOC_8H_{17}$		—	0,31	0,36	0,33
$CH_2=C(CH_3)COOCH_3$	$CH_2=CHOCH(CH_3)_2$		0,23	0,29	0,31	0,26
$CH_2=C(CH_3)COOCH_3$	$CH_2=CHOC_6H_5$		0,46	0,4	0,46	0,44
$CH_2=CHCOOCH_3$	$CH_2=CHOC_2H_5$		0,51	0,56	0,58	0,55
$CH_2=CHCOOCH_3$	$CH_2=CHOC_4H_9$		0,6	0,65	0,55	0,6
$CH_2=CHCOOCH_3$	$CH_2=CHOC_6H_5$		0,59	0,55	0,56	0,57

Furthermore, it is assumed that the concentrations of the radicals does not change during reactions (2) and (3); therefore, these reactions can be considered to be first order. In this case the rate of disappearance of the monomers M_1 and M_2 can be expressed by the following equations:

$$-\frac{dM_1}{dt} = K_4 M_1 \quad (4) \text{ and } -\frac{dM_2}{dt} = K_2 M_2 ; \tag{5}$$

dividing (4) by (5):

$$\frac{dM_1}{dM_2} = \frac{K_4 M_1}{K_2 M_2} . \tag{6}$$

At a given moment Eq. (6) can be written in the form

$$\frac{m_1}{m_2} = \frac{K_4 M_1}{K_2 M_2} , \tag{7}$$

where m_1 is the number of vinyl ester units in the copolymer in mole %, and m_2 is the number of vinyl ether units in the copolymer in mole %.

If the ratio K_4/K_2 is designated r_3, Eq. (7) transforms into

$$r_3 \frac{M_1}{M_2} = \frac{m_1}{m_2} ; \tag{8}$$

for our case $m_1 = m_2 = 50$ mole % and Eq. (8) transforms into

$$r_3 \frac{M_1}{M_2} = 1,$$

from where

$$r_3 = \frac{M_2}{M_1}$$

substituting, for example, the values for methylacrylate and vinylethyl ether:

$$r_3 = \frac{M_2}{M_1} = \frac{90,9}{9,1} \approx 10,$$

i.e., the rate of addition of methylacrylate to the vinyl ether radical is ten times faster than the rate of addition of the vinyl ether to the vinyl ester radical.

SUMMARY

1. Vinyl ethers do not augment the polymerization chain by means of addition to their own radicals during copolymerization, but are able to polymerize alone by the radical mechanism.

2. An equation was developed for the relationship between the starting concentration of vinyl ether in the reaction medium and the number of vinyl ether units in the copolymer.

3. The relative rate constant for addition to "foreign" radicals during copolymerization of methylacrylate and vinylethyl ether was calculated.

4. The differential and integral copolymer composition equations are inapplicable for calculating the relative activities of vinyl ether radicals during copolymerization with the methyl ester of acrylic or methacrylic acid.

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BRIEF COMMUNICATIONS

CONCERNING INTRAMOLECULAR TRANSACETALIZATION WITH THE FORMATION OF 1,3-DIOXANES

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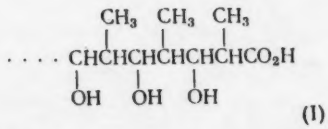
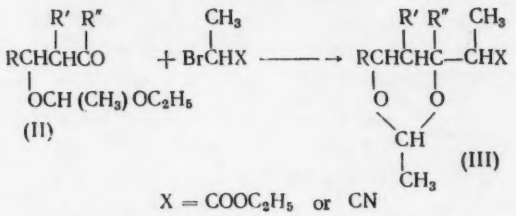
For the purpose of studying routes for the synthesis of polyhydroxy acids of type (I),



(I)

lying at the base of the skeleton of erythromycin and some other macrolides, we investigated the possibility of obtaining β,δ-dihydroxy acids by the Reformatskii condensation of β-hydroxycarbonyl compounds with α-bromopropionic ester. Since the condensation of the hydroxycarbonyl compounds as such proceeds unsatisfactorily, we first acetalized the hydroxyl group using vinylethyl ether. The obtained acetals (II) readily entered into the Reformatskii reaction, and here we isolated the intramolecular transacetalization products – 1,3-dioxanes of type (III).



X = $COOC_2H_5$ or CN

With this technique we obtained from propionaldol acetal (II) (R = C_2H_5, R' = CH_3, R" = H) the ethyl ester and nitrile of 3,5-ethylidenedioxy-2,4-dimethylheptanoic acid (III) (R = C_2H_5, R' = CH_3, R' = H, X = $COOC_2H_5$ or CN), while from 4-pentanol-2-one acetal (II) R = R" = CH_3, R' = H) we synthesized the ethyl ester of 3,5-ethylidenedioxy-2,3-dimethylhexanoic acid (III) (R = R" = CH_3, R' = H, X = $COOC_2H_5$). The structure of the obtained compounds was adopted on the basis that none of them contain the OH group (based on the data of the infrared spectra and determination of active hydrogen), but that they represent the acetals of acetaldehyde (the latter is cleaved under acid hydrolysis conditions); the infrared spectra exhibit a doublet in the 1150-1090 cm^{-1} region, which is characteristic for the C–O–C–O–C grouping [1, 2]).

EXPERIMENTAL

Propionaldol acetal. To 58 g (0.5 mole) of freshly distilled propionaldol were added 0.02 ml of concd. HCl and 72 g (1 mole) of vinyl ethyl ether. The reaction was accompanied by a warming up of the mixture (up to 50°). The mixture was allowed to stand at room temperature for 70 hr, after which it was diluted with 50 ml of ether; the ether solution was washed with 5% potassium carbonate solution, then with water, and dried over magnesium sulfate. After removal of the solvent and excess vinylethyl ether by distillation the residue was vacuum-distilled twice. We obtained 53.7 g (57%) of propionaldol acetal with b. p. 114-116° (30 mm); $n^{20}D$ 1.4286; d^{20}_4 0.9446; found MR 51.34; calculated MR 51.68. Found: C 64.16, 63.96; H 10.81, 10.79%. $C_{10}H_{20}O_3$. Calculated: C 63.80; H 10.71%.

4-Pentanol-2-one acetal. From 204 g (2 mole) of 4-pentanol-2-one and 288 g (4 moles) of vinylethyl ether under the above described conditions we obtained 230 g (66%) of 4-pentanol-2-one acetal with b. p. 88-89° (20 mm);

$n^{20}D$ 1.4210; d^{20}_4 0.9407; found MR 46.97; calculated MR 47.01. Found: C 61.95, 61.78; H 10.10, 10.30%. $C_9H_{18}O_3$. Calculated: C 62.04; H 10.41%.

Reaction of propionaldol acetal with ethyl α-bromopropionate. A mixture of 27.15 g (0.15 mole) of ethyl α-bromopropionate and 9.4 g (0.05 mole) of propionaldol acetal in 50 ml of benzene was added in 40 min to a mixture of 9.81 g (0.15 mole) of fine zinc turnings and 50 ml of dry benzene under gentle reflux of the solvent.* The mixture was then refluxed for another 2 hr, after which it was cooled and stirred for 30 min with 75 ml of 3 N hydrochloric acid. The organic layer was separated, while the water layer was extracted 3 times with benzene, and then the combined extracts were washed with water, 10% sodium bicarbonate solution, again with water, and finally dried over magnesium sulfate. After distilling off the benzene, followed by a 2-fold distillation of the residue in vacuo, we obtained 4.95 g (40%) of the ethyl ester of 3,5-ethylidenedioxy-2,4-dimethylheptanoic acid with b. p. 74-78° (1 mm); $n^{20}D$ 1.4430; d^{20}_4 0.9989; found MR 64.85; calculated MR 64.97; found mole wt. (Rast) 235, 243; calculated 244. Found: C 64.16, 63.92; H 9.97, 9.87%. $C_{13}H_{24}O_4$. Calculated: C 63.90; H 9.92%.

Reaction of 4-pentanol-2-one acetal with ethyl α-bromopropionate. Using the above described conditions, from 8.71 g of 4-pentanol-2-one acetal, 27.15 g of ethyl α-bromopropionate and 9.81 g of zinc turnings we obtained, after fractional distillation in vacuo, 3.25 g (28%) of the ethyl ester of 3,5-ethylidenedioxy-2,3-dimethylhexanoic acid with b. p. 60-61° (1 mm); $n^{20}D$ 1.4412; d^{20}_4 1.0049; found MR 60.54; calculated MR 60.36; found mole wt. (Rast) 226, 235; calculated 230. Found: C 62.63, 62.83; H 9.41, 9.55%. $C_{12}H_{22}O_4$. Calculated: C 62.58; H 9.63%.

Reaction of propionaldol acetal with α-bromopropionitrile. Several drops of α-bromopropionitrile were added to a refluxing mixture of 18.82 g (0.1 mole) of propionaldol acetal, 8 g (0.12 mole) of zinc turnings and 0.3 g of mercuric chloride in 25 ml of tetrahydrofuran (see [3]). A stormy reaction began immediately. The heating was stopped and the remainder of the α-bromopropionitrile (a total of 16.1 g; 0.12 mole) was added in 10 min. All of the zinc dissolved in 15 min, after which the reaction mixture was heaed for another 30 min. After cooling, 75 g of ice and 25 ml of glacial acetic acid were added, after which the mixture was stirred for 30 min, and then 30 ml of benzene was added. The organic layer was separated, the water layer was extracted 3 times with benzene, and the combined benzene extracts were washed with water, 10% sodium bicarbonate solution, again with water, and finally dried over magnesium sulfate. After distilling off the benzene, followed by vacuum-distillation of the residue, we obtained 8.26 g (42%) of the nitrile of 3,5-ethylidenedioxy-2,4-dimethylheptanoic acid with b. p. 79-81° (1 mm); $n^{20}D$ 1.4520; d^{20}_4 0.9885; found MR 54.00; calculated MR 53.90; found mole wt. (Rast) 200, 201; calculated 197. Found: C 67.00, 66.82; H 9.91, 9.93; N 6.95, 6.79%. $C_{11}H_{19}NO_2$. Calculated: C 66.97; H 9.96; N 7.11%.

Acid hydrolysis of 1,3-dioxanes. A solution of 0.5 g of ethyl 3,5-ethylidenedioxy-2,4-dimethylheptanoate and 0.5 g of 2,4-dinitrophenylhydrazine in 1 ml of concd. sulfuric acid and 10 ml of ethyl alcohol was heated for 5 min. After cooling, filtration, and chromatographing the precipitate on Al_2O_3 we isolated 0.3 g of acetaldehyde 2,4-dinitrophenylhydrazone, identified by the mixed melting point test (m. p. 167-168°) and by chromatographing on paper (R_f 0.18 in the system decalin/dimethylformamide [4]: paper – "Leningrad rapid"). Analogous results were obtained in the hydrolysis of 3,5-ethylidenedioxy-2,3-dimethylhexanoic acid and the nitrile of 3,5-ethylidenedioxy-2,4-dimethylheptanoic acid.

SUMMARY

2-Methyl-1,3-dioxanes were isolated when the (α-ethoxyethyl) ethers of β-hydroxycarbonyl compounds were subjected to the Reformatskii reaction.

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* The reaction and subsequent distillation were both run in a current of dry nitrogen; the reaction was initiated by the addition of 2 ml of an ether solution of C_2H_5MgBr.

CONCERNING THE STRUCTURE OF THE AMINATION PRODUCTS OF NICOTINE

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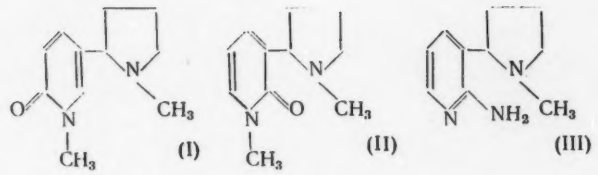
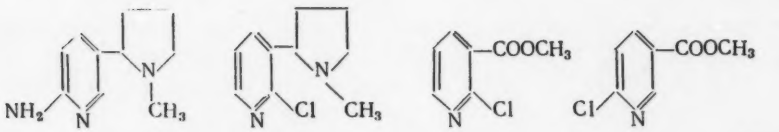
Recently it was shown by one of us with Kiseleva [1] that the product of the oxidation of nicotine Py-methiodide was potassium ferricyanide; the so-called N-methylnicotone, has structure (I), and not (II), as was assumed by Karrer and Takahashi [2].



(I) (II) (III)



(IV) (V) (VI) (VII)

The only reason for Karrer and Takahashi assuming such a structure was the fact that the chloronicotinic acid, formed from N-methylnicotone, had the same melting point (192°) as the acid isolated by Chichibabin and Kirsanov [3] in the oxidation of 2-chloronicotine (V). The latter, in turn, was obtained from an aminonicotine with m. p. 125°, to which they assigned structure (III). An inconsistency appears when all of these data are compared, since only 6-chloronicotinic acid (m. p. 199°), and not 2-chloronicotinic acid (m. p. 193°), can be formed from (I). Although the results of studying the infrared spectra [4] and the alkylation products of the aminonicotines [5] were in harmony with the viewpoint of Chichibabin and Kirsanov, it seemed expedient to again return to the question of the structure of these bases. With this in mind we used the method described in [3] to obtain the chloronicotines from the two aminonicotines, which were then converted to the chloronicotinic acids, and the latter, by treatment with diazomethane, were then converted to the corresponding methyl esters. The ester, obtained as a result of this sequence of transformations from the aminonicotine with m. p. 125°, had the same constants as the methyl ester of 2-chloronicotinic acid (VI) [6, 7]. On the other hand, the aminonicotine with m. p. 66°, to which Chichibabin and Kirsanov had assigned structure (IV), gave an ester with m. p. 86.3-86.7°; the methyl ester of 6-chloronicotinic acid (VII) has the same melting point [7, 8]. We obtained the corresponding amides from these esters. Here it was found that the amide, for which the aminonicotine with m. p. 125° served as the starting compound, had m. p. 164.1-164.7°, whereas the amide, corresponding to the aminonicotine with m. p. 66°, had m. p. 211.5-212.5°. According to the literature, the amide of 2-chloronicotinic acid [9, 10] has m. p. 164-165°, while the amide of 6-chloronicotinic acid [11, 12] has m. p. 210-211°. The properties of the indicated two series of derivatives, as compounds where in one case the halogen is located sterically close to the function containing the CO group, while in the other case it is at some distance from this function, are confirmed by the spectral data.

As can be seen from the presented curves, for all of the "ortho" derivatives the absorption coefficient in the ultraviolet region is considerably below that for the "para" derivatives; some shift toward longer wavelengths is also

	Name of compound	M.p. (B.p.), °C		d_4^{20}	n_D^{20}	MR		C, %		H, %		Cl, %	
		found	literature data			found	calc.	found	calc.	found	calc.	found	calc.
Transformation products of aminonicotine with m.p. 125°	2-Chloronicotine	112,3—113,3 (4 mm)	268—269 (740 mm) [3]	1,145	1,5425	54,07	54,05	61,2	61,07	6,72	6,66	17.89	18,03
	Picrate**	138—139						45,7	45,49	4,22	4,26	8,28	7,9
	2-Chloronicotinic acid	192,5—193***	193 [3,7]					45,75	45,74	2,55	2,56		
	Methyl ester	102,5 (4 mm)	87—86 (3mm) [6]	1,325	1,5368	40,43	40,08	49,1	49,0	3,51	3,52	20,75	20,67
	Amide	164,1—164,7	164—165 [9]										
Transformation products of aminonicotine with m.p. 66°	6-Chloronicotine	138,5—139,5 (8mm)	270—271 (742 mm) [3]	1,139	1,5418	54,28	54,05	61,11	61,07	6,66	6,66		
	Picrate**	158—159						45,11	45,13	3,87	3,78	8,31	8,32
	6-Chloronicotinic acid	198—199***	199 [3,7]					45,57	45,74	2,7	2,56	22,77	22,51
	Methyl ester	86,3—86,7	86—89 [7]					48,99	49,0	3,64	3,52	20,62	20,67
	Amide	211,5—212,5	210—211 [12]										

* $C_{10}H_{13}ClN_2 \cdot C_6H_3N_3O_7 \cdot \frac{1}{2} C_2H_5OH$.

** $C_{10}H_{13}ClN_2 \cdot C_6H_3N_3O_7$.

*** The capillary was introduced into the apparatus 10° below the melting point.

observed for the latter. This is in agreement with the fact that a close proximity of the halogen to the function causes the COOH group to come out of the plane of the ring, which leads to a decrease in the extent of conjugation. As a result, it can be truthfully stated that the structures, established by Chichibabin and Kirsanov for the aminonicotines, are in full agreement with the experimental data. We are of the opinion that an error exists in the experimental work of Karrer and Takahashi, apparently caused by the fact that the difference in the melting points of the chloronicotinic acids is small, and also because the acids have ill-defined melting points. When heated in a capillary the acids decompose, and the decomposition temperature depends on the rate of heating. However, the mixed melting point of these acids is depressed. The constants of the obtained compounds are given in the table.

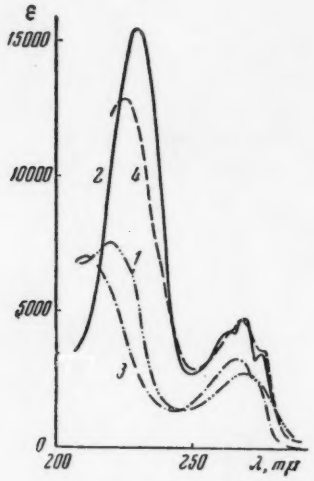


Fig. 1. Ultraviolet spectra of methyl esters (1, 2) and amides (3, 4) of: 1) 2-chloronicotinic acid; 2) 6-chloronicotinic acid (in heptane); 3) 2-chloronicotinic acid; 4) 6-chloronicotinic acid (in alcohol.

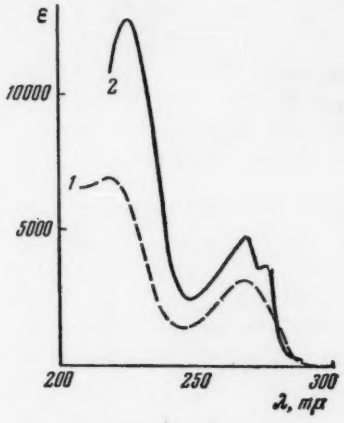


Fig. 2. Ultraviolet spectra of: 1) 2-chloronicotinic acid; 2) 6-chloronicotinic acid (in alcohol).

The absorption spectra of the compounds were measured in the Optical Laboratory of the Institute by V. A. Petukhov, for which the authors wish to thank him.

SUMMARY

The conclusion of Chichibabin and Kirsanov relative to the structure of the amination products of nicotine is in full agreement with the experimental data. An inconsistency exists between the results obtained by Karrer and Takahashi [2] and the later experimental facts relating to this problem.

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THE CATALYTIC SYNTHESIS OF 1,5-DIKETONES

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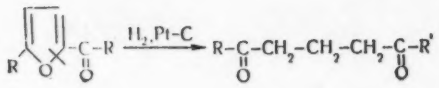
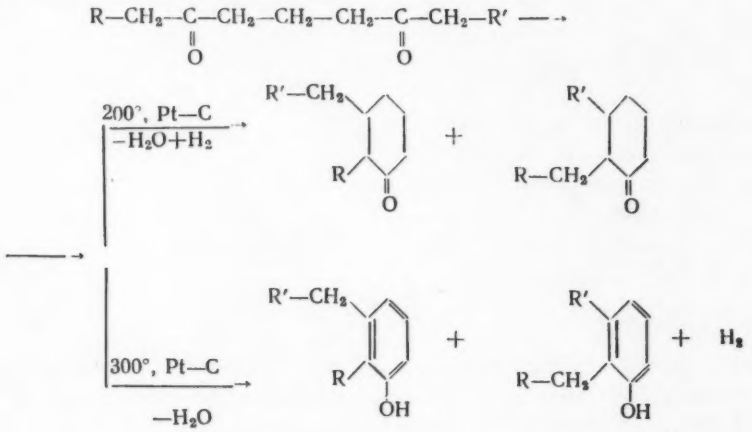
As we had previously shown [1, 2], the hydrogenation of 2-alkyl-5-acylfurans on platinized carbon at 200° goes with the formation of the corresponding alkylcyclohexanones, whereas at 300° the main reaction products are alkylphenols. We expressed the theory that the formation of these compounds goes through the 1,5-diketone stage via hydrogenation of the furan ring at the C–O bond, adjacent to the carbonyl-containing substituent.



However, under the indicated conditions the intermediately formed diketones were completely subjected to further transformations and we could not isolate them.



The theory that 1,5-diketones are formed in the hydrogenolysis of 2-alkyl-5-acylfurans was confirmed when we ran the hydrogenolysis of the 2-alkyl-5-acylfurans at 200° on 10% platinized carbon, which had lost to a considerable degree it activity relative to the cyclization of diketones, and isolated the corresponding diketones from the catalyzate. However, the yield of the diketones did not exceed 5-10% of theory. As might be expected, when we took 10% platinized asbestos as the catalyst in subsequent studies it proved that this catalyst was less active relative to the cyclization of diketones, and when we ran the hydrogenolysis of 2-alkyl-5-acylfurans on it at 200° we were able to isolate the corresponding diketones in 30-35% yield based on the catalyzate. When the complexity of the usual methods for the synthesis of 1,5-diketones is considered, the method proposed by us for the catalytic synthesis of these compounds from 2-alkyl-5-acylfurans possesses not only theoretical, but also practical interest.

The starting 2-alkyl-5-acylfurans were obtained by the acylation of the proper 2-alkylfurans with either acetic or propionic anhydride in the presence of phosphoric acid [3]; the compounds had the following properties:

1) 2-Methyl-5-acetylfuran, b. p. 68-69° (7 mm); $n^{20}D$ 1.5090; d^{20}_4 1.0655; yield 35-40%; 2) 2-n-propyl-5-acetylfuran, b. p. 110-112° (20 mm); $n^{20}D$ 1.5011; d^{20}_4 1.0102; yield 35-40%; 3) 2-ethyl-5-propionylfuran, b. p. 107-108° (18 mm); $n^{20}D$ 1.5000; d^{20}_4 1.0512; yield 28-30%; 4) 2-n-butyl-5-acetylfuran, b. p. 142-143° (3 mm); $n^{20}D$ 1.4952; d^{20}_4 0.9827; yield 30-40%. The catalyst, 10% Pt on asbestos, was prepared by impregnating asbestos

with a solution of chloroplatinic acid and subsequent reduction in the catalyst tube at 300-350°. The asbestos was first treated with 20% NaOH solution, and then with concd. nitric acid on the water bath, after which it was washed with water, dried, and ignited in a crucible at 600°.

The hydrogenation was run in an apparatus of the flow type at 200° and atmospheric pressure. The starting substance was fed into the catalyst tube at a space velocity of 0.1 hr^{-1}. The catalyzates were vacuum-distilled through a column having an efficiency of 30 theoretical plates. The following diketones were isolated:

1) From the 2-methyl-5-acetylfuran catalyzate we obtained 2,6-heptanedione with b. p. 112-114° (25 mm); m. p. 32-33°; $n^{40}D$ 1.4245; dioxime, m. p. 87°; the yield was 28%; 2) from the 2-ethyl-5-propionylfuran catalyzate we obtained 3,7-nonanedione with b. p. 82° (6 mm); m. p. 37-38°; $n^{55}D$ 1.4252; dioxime, m. p. 92-93°; yield 32%; 3) from the 2-propyl-5-acetylfuran catalyzate we obtained 2,6-nonanedione with 84-85° (2 mm); m. p. 36-37°; $n^{50}D$ 1.4264; dioxime, m. p. 93°; the yield was 30%; 4) from the 2-butyl-5-acetylfuran catalyzate we obtained 2,6-decanedione with b. p. 100-101° (3 mm); m. p. 39-40°; $n^{50}D$ 1.4272; dioxime, m. p. 98°; the yield reached 38%. All of the diketones tend to crystallize slowly, with difficulty; the corresponding dioximes were obtained by the Fargher and Perkin method [4].

SUMMARY

1. 1,5-Diketones are the first products of the hydrogenolysis of 2-alkyl-5-acylfurans on platinized carbon or platinized asbestos at 200-300° and atmospheric pressure.

2. A method was proposed for the catalytic synthesis of 1,5-diketones from 2-alkyl-5-acylfurans.

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DIALKYLALUMINUM DERIVATIVES OF SATURATED AND UNSATURATED ACIDS

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In recent years a definite interest has been displayed in obtaining the methacrylates and acrylates of trialkyltin [1-3] and germanium [4], and also the polymers and copolymers based on them [4-6]. In this connection it seemed of interest to obtain the methacrylates and acrylates of dialkylaluminum and make a study of their properties. Individual communications [7, 8] exist in the literature relative to obtaining organoaluminum compounds of type $(RCOO)_xAl(OR')_{3-x}$, where R = CH_3, C_2H_5, $C_{15}H_{31}$, etc., R' – i-C_3H_7, x – 1, 2, 3, but compounds of type $(RCOO)_xAlR'_{3-x}$ are not described in the literature. Attempts to obtain the salts of dialkylaluminum with aliphatic acids by reacting the potassium salts of the acids with dialkylaluminum chlorides led to negative results, apparently because of the formation of organoaluminum complexes with the KCl; for this reason we reacted the trialkylaluminum with the free saturated and unsaturated acids in accordance with the following scheme:

$$RCOOH + AlR'_3 \longrightarrow RCOOAlR'_2 + R'H$$

The reaction was run in either n-hexane or benzene with vigorous stirring, and here the liberation of saturated hydrocarbons in amounts close to the calculated were observed during reaction. With this procedure we obtained the following salts of dialkylaluminum with saturated acids – diisobutylaluminum acetate and diisobutylaluminum propionate – while employing unsaturated acids we obtained diethylaluminum methacrylate, diethylaluminum acrylate, and diisobutylaluminum methacrylate. The obtained substances were clear, colorless, slightly viscous oils that distill with ease, and which fume and at times even catch fire in the air. The constants of the compounds are given in the table.

Physical Constants of Dialkylaluminum Salts

R	R'	B.p., °C (p = = mm of Hg)	Yield, %	Found Al, %	Calculated Al, %
CH_3—	i-C_4H_9	145—146(3)	85	13,52 13,15	13,47
C_2H_5—	i-C_4H_9	148—149(2)	85	12,11 12,10	12,41
$CH_2=C(CH_3)$—	i-C_4H_9	156—157(2)	75	*	*
$CH_2=C(CH_3)$—	C_2H_5	126—127(3)	59	15,71 15,75	15,88
$CH_2=CH$—	C_2H_5	131—133(6)	51	17,40	17,30

* Found: C 63.75; H 10.57%. Calculated: C 63.71; H 10.18%.

The salts of dialkylaluminum with the unsaturated acids are capable of being polymerized either employing heat or in the presence of initiators, for example, azobisisobutyronitrile, forming clear viscous polymers that are very difficultly soluble in organic solvents, but are capable of swelling in certain polar media (for example, amyl acetate or dimethylformamide). The salts of dialkylaluminum with the unsaturated acids copolymerize readily with methylmethacrylate or styrene in all proportions (1:0.5, 1:1, 1:2, 1:4, etc.), forming hard, clear, glassy polymers that are practically insoluble in organic solvents. The homopolymers decompose in the air, while the copolymers do not change in the air when stored for a short time.

EXPERIMENTAL

All of the reactions and operations with the organoaluminum compounds were conducted in an atmosphere of pure nitrogen.

Diisobutylaluminum propionate. With cooling in a water bath, a solution of 6 g (0.083 mole) of propionic acid in n-hexane was added to 16 g (0.083 mole) of triisobutylaluminum in either n-hexane or benzene solution. After this the mixture was heated at 70-80° for 2 hr to complete the reaction. After removal of the solvent by distillation the product was vacuum-distilled, collecting the fraction with b. p. 148-149° (2 mm). We obtained 147 g (85.0% yield) of the compound.

Diethylaluminum methacrylate. With water cooling, a solution of 9 g (0.14 mole) of methacrylic acid in n-hexane was added to a solution of 16 g (0.14 mole) of triethylaluminum in n-hexane. The solvent was removed by distillation, while the reaction mixture was vacuum-distilled in the presence of a stabilizer (cuprous chloride), collecting the fraction with b. p. 126-127° (3 mm). We obtained 10.2 g (59.0% yield) of the compound.

SUMMARY

Some salts of dialkylaluminum with both saturated and unsaturated acids were obtained. The salts of dialkylaluminum with unsaturated acids are capable of being polymerized and copolymerized in the presence of azobisisobutyronitrile as initiator.

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THE REDUCTION OF CYCLOHEXANONE ON SKELETAL ZINC CATALYST UNDER PRESSURE

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Previously it was shown that cyclohexanone is reduced with difficulty on zinc catalyst at atmospheric pressure: the reaction did not go at 50°, while at 100° the yield of cyclohexanol was only 17% of the theoretical. There was reason to believe that the low activity of zinc in this reaction was due to the insufficient concentration of hydrogen on the catalyst [1]. It was natural to expect that the concentration of active hydrogen would increase if the hydrogenation was run under pressure, and this should lead to an increase in both the reaction rate and the yield of cyclohexanol. For this reason we made a study in the present paper of the effect of pressure on the extent to which cyclohexanone hydrogenates on zinc catalyst at various temperatures.

Expt. No.	Temperature, °C (p, atm)	Reaction time, min	Comp. of catalyz., % cyclohexanol	cyclohexanone	cyclohexene
1	50(50)	30	6	89	3
2	70(50)	30	12	78	7
3	90(50)	30	21	66	10
4	110(50)	30	30	53	13
5	130(50)	30	42	36	17
6	50(100)	15	71	13	13
7	75(100)	15	76	6	16
8	100(100)	15	79	2	17
9	125(100)	15	80	0	18
10	125(100)	30	73	0	25
11	125(100)	60	62	0	36

EXPERIMENTAL

The experiments were run in a rotated 0.25 liter autoclave. The catalyst was prepared by the method described in [2]. The catalyst had a volume of 50 ml and it was used only once. Freshly distilled cyclohexanone with b. p. 155° and $n^{20}D$ 1.4500 was used for the reaction. The obtained catalyzates were dried over sodium sulfate and then subjected to fractional distillation. The fraction with b. p. 82-84° represented cyclohexene ($n^{20}D$ 1.4453; d^{20}_4 0.8108). One mole of hydrogen was absorbed when the cyclohexene was hydrogenated on skeletal nickel at 20°. The fraction with b. p. 155-160° was a mixture of cyclohexanol and unreacted cyclohexanone. This fraction was analyzed for the amount of cyclohexanone by the oxime method. The yield of cyclohexanol was calculated by difference.

The results of Expt. Nos. 1-5, conducted at an initial hydrogen pressure of 50 atm and a reaction time of 30 min, are given in the table. From the table it can be seen that under these conditions the hydrogenation of cyclohexanone begins at a temperature as low as 50°. The yield of cyclohexanol increases with increase in the temperature and at 130° reaches 42%. When the initial hydrogen pressure is increased to 100 atm the yield of cyclohexanol increases even more, and at 50° and a reaction time of 15 min reaches 71%. Further increase in the temperature has little effect on the yield of cyclohexanol (Expt. Nos. 6-8). The hydrogenation of cyclohexanone, both at atmospheric and at elevated pressure, is complicated by the dehydration of the formed cyclohexanol. The dehydration takes place even at 50-75°, increases with increase in the temperature, and is probably caused by the presence of aluminum and zinc oxides in the skeletal zinc catalyst. The promoting action of zinc oxide in the dehydration of alcohols on aluminum oxide has also been observed in other studies, for example, in [3]. The data on Expt. Nos. 1-8 make it possible to assume that the substantial dehydration of the formed cyclohexanol to cyclohexene under our conditions is due to the longer time of contact with the catalyst. Experiment Nos. 9-11, where the reaction time was varied, confirmed this assumption. When the reaction time was increased from 15 to 60 min the yield of cyclohexene rose from 18 to 36%, while the yield of cyclohexanol decreased from 80 to 62%.

SUMMARY

1. A high yield of cyclohexanol is obtained when cyclohexanone is hydrogenated on zinc catalyst under pressure.

2. The main reaction is complicated by the secondary dehydration of the formed cyclohexanol to cyclohexene.

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SOME CARBONYLCHROMIUM ARENES

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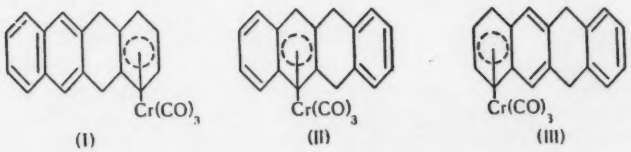
The chemistry of the π-complexes of the transition metals [1, 2] and, in particular, of the carbonylarene compounds of type $XArMe(CO)_3$ (X = substituent, and Me = metal) has received extensive development in recent years. We investigated the reaction of $Cr(CO)_6$ with compounds containing several aromatic nuclei (diphenylmethane, trans-stilbene, tolane, tetracene, and 5,12-dihydrotetracene). All of the experiments were run in an atmosphere of pure nitrogen. When a solution of 1.68 g (0.010 mole) of diphenylmethane and 1.11 g (0.005 mole) of $Cr(CO)_6$ in 50 ml of dibutyl ether was heated under reflux for 5 hr we obtained 0.35 g (23% of the theoretical yield) of tricarbonylchromiumdiphenylmethane as a pale yellow product. The substance was purified by chromatographing on Al_2O_3 (eluant – a 1:1 mixture of heptane and benzene), after which it was recrystallized from the same mixture. The pure compound had m. p. 98-99° in a sealed capillary. Found: C 63.40, 63.30; H 4.17, 4.05; Cr 17.04, 17.12%. $C_{16}H_{12}O_3Cr$. Calculated: C 63.17; H 3.94; Cr 17.10%. In a nitrogen atmosphere tricarbonylchromiumdiphenylmethane is stable up to 200°. The reaction of diphenylmethane with excess $Cr(CO)_6$ also yields only tricarbonylchromiumdiphenylmethane. When a solution of 0.8 g (0.0044 mole) of trans-stilbene and 0.48 g (0.0022 mole) of $Cr(CO)_6$ in 40 ml of dibutyl ether was heated under reflux for 4 hr we obtained 0.33 g (48% of theory) of tricarbonylchromiumstilbene. The substance was purified on Al_2O_3 (eluant – a 1:1 mixture of benzene and heptane), after which it was recrystallized from the same mixture. The compound was obtained as red crystals with m. p. 130-131.5° in a sealed capillary.* Found: C 64.63, 64.70; H 3.82, 3.74; Cr 16.34, 16.35%. $C_{17}H_{12}O_3Cr$. Calculated: C 64.57; H 3.79; Cr 16.46%. The reaction went differently with tolane. Only the starting substances were isolated when we heated a mixture of 0.2 g (0.0012 mole) of tolane and 0.37 g (0.0017 mole) of $Cr(CO)_6$ in 20 ml of dibutyl ether under reflux for 4 hr. Hexaphenylbenzene was obtained when the same quantities of tolane and $Cr(CO_6)$ in 20 ml of decalin were heated under reflux for 3 hr. After recrystallization from benzene, the compound had m. p. 432°. Literature data: b. p. 426-427° [4]. Found: C 94.22, 94.30; H 5.70, 5.68%. $C_{42}H_{30}$. Calculated: C 94.38; H 5.61%. Besides hexaphenylbenzene, two other chromium-free compounds were obtained, but their amounts were too small to permit identification. The formation of hexaphenylbenzene is not astonishing. It is known that acetylenes are converted to the trimers when heated with the carbonyls of the transition metals [5]. Evidently this reaction goes more rapidly than does the reaction of the carbonyl with the π-electron system of aromatic rings. Despite numerous attempts, we were unable to obtain the chromium derivative of tetracene. This is in harmony with the data of Fischer [6], who obtained tricarbonylchromiumanthracene with difficulty and made the remark that the chromium derivatives are formed with constantly greater difficulty as the number of linearly condensed rings increases.

5,12-Dihydrotetracene behaved in an entirely different manner. A solution of 1 g (0.00436 mole) of dihydrotetracene and 1.42 g (0.00654 mole) of $Cr(CO)_6$ in 80 ml of decalin was heated for 4 hr at 185-190°. As a result, we obtained 1 g (62.5% of theory) of pale yellow tricarbonylchromiumdihydrotetracene. The compound was purified by chromatographing on Al_2O_3 (eluant – a 1:1 mixture of benzene and heptane), followed by recrystallization from the same solvent mixture, after which it had m. p. 184.5-185° in a sealed capillary. Found: C 68.98, 68.80; H 3.96, 3.74; Cr 14.13, 14.40%. $C_{21}H_{14}O_3Cr$. Calculated: C 68.87; H 3.82; Cr 14.20%. Tricarbonylchromiumdihydrotetracene can also be obtained in dibutyl ether, but the yield is lower in this case. Dihydrotetracene is formed in the thermal decomposition (~200°) of tricarbonylchromium-5,12-dihydrotetracene. When 0.1 g of tricarbonylchromiumdihydrotetracene was refluxed with 1 ml of pyridine for 1 hr we isolated dihydrotetracene (yield 71.4% of theoretical) with m.p. 209-210°. Literature data: m.p. 212° [7]. We also recovered traces of the starting compound.

* While doing the work we learned that tricarbonylchromiumstilbene was obtained [3] by exchange reaction between stilbene and tricarbonylchromiumtoluene; the compound had m. p. 131-132°.

We attempted to dehydrogenate tricarbonylchromiumdihydrotetracene to tricarbonylchromiumtetracene under the conditions used to convert dihydrotetracene to tetracene [7]. However, the heating of the tricarbonylchromium derivative with chloranil in either glacial acetic acid or benzene led to a rapid and complete decomposition to dihydrotetracene and the conversion of the latter to tetracene. Three tricarbonylchromiumdihydrotetracene isomers are possible:



(I) (II) (III)

At the present time data are lacking that would permit judging the structure of the obtained isomer. True, the pale yellow color and high stability of this compound speak in favor of structure (I), since tricarbonylchromiumnaphthalene has a red color and is unstable [8].

We made numerous attempts to introduce two chromium atoms into the dihydrotetracene molecule. The use of excess $Cr(CO)_6$, raising the temperature, and increasing the reaction time all gave negative results. When a mixture of tricarbonylchromiumdihydrotetracene and $Cr(CO)_6$ in decalin was heated under reflux for 1 hr we also obtained only the unreacted starting compounds. As a result, in not a single instance were we able to introduce more than one chromium atom into the molecule when multinuclear aromatic compounds were reacted with $Cr(CO)_6$. This cannot be explained by the instability of the bis-tricarbonylchromium compounds, since while doing the present work a paper [3] was published on the synthesis of some bis(tricarbonylchromium) arenes by reacting the appropriate aromatic compounds with either tricarbonylchromiumbenzene or tricarbonylchromiumtoluene. In connection with this it is interesting to mention that we were unable to obtain the tricarbonylchromium derivatives of benzyl and phenylferrocene. In the solid state all of the tricarbonylchromiumarenes obtained by us were completely stable in the air. In solutions they gradually decomposed at room temperature, depositing an inorganic precipitate. All of the compounds synthesized by us were soluble in cold concentrated H_2SO_4, in which connection they begin to decompose almost immediately with the evolution of gas. The decomposition became violent on heating.

The infrared spectra* of all of the tricarbonylchromium compounds (including the earlier described tricarbonylchromiumbenzene [8] and tricarbonylchromiumtetralin [9]) contain two maxima at ~1950 cm^{-1} and ~1870 cm^{-1} in the carbonyl region, which is characteristic for such compounds [10].

SUMMARY

1. The reaction of hexacarbonylchromium with diphenylmethane, trans-stilbene and 5,12-dihydrotetracene gave tricarbonylchromiumdiphenylmethane, tricarbonylchromiumstilbene and tricarbonylchromium-5,12-dihydrotetracene.

2. Hexaphenylbenzene is formed when tolane is reacted with $Cr(CO)_6$.

3. Tetracene does not react with $Cr(CO)_6$.

4. In not a single instance were we able to obtain bis-tricarbonylchromium compounds.

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REACTION OF TRIISOBUTYLBORON AND DIBORANE WITH STYRENE

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In recent years a number of papers have been published on the addition of diborane to α-olefins [1, 2]. It was shown that here the boron atom adds to the terminal carbon atom of the α-olefin and the oxidation of the obtained borontrialkyls with alkaline hydrogen peroxide leads exclusively to the formation of primary alcohols. Analogous results were obtained when the complex of pyridine with diborane was used [3], and also when the lower olefin of the borontrialkyls was displaced by the higher α-olefins [2]. In view of the definite analogy existing between boron and aluminum derivatives in the reactions with α-olefins, it seemed of interest to us to make a more detailed study of the reaction of triisobutylboron and diborane with styrene, since in the case of styrene, in contrast to other α-olefins, as has been found by one of the present authors and Gavrilenko [4], and also by Natta and co-workers [5], when it is reacted with triisobutylaluminum and dialkylaluminum hydride the aluminum atoms adds to both the α- and β-carbon atoms of the vinyl group. It proved that both the reaction of displacing styrene by triisobutylboron and the addition of diborane lead to obtaining both possible products:

$$C_6H_5CH{=}CH_2 + (i\text{-}C_4H_9)_3B \longrightarrow (C_6H_5CH_2CH_2)_3B + (C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}H)_3B + C_4H_8$$

$$C_6H_5CH{=}CH_2 + B_2H_6 \longrightarrow (C_6H_5CH_2CH_2)_3B + (C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}H)_3B$$

The displacement reaction was run at 150-180°. Oxidation of the obtained triphenylethylboron gave a mixture of the α- and β-phenylethyl alcohols in high yield. The composition of the mixture was determined by two different procedures: by oxidation with chromium trioxide and isolation of the acetophenone as the 2,4-dinitrophenylhydrazone, and by employing infrared spectrometry. The amount of phenylmethylcarbinol in the mixture was about 15%. The addition of diborane to sytrene was run in tetrahydrofuran solution. The reaction product obtained here was divided into two parts; one part was immediately subjected to oxidation, while the other part, after removal of the tetrahydrofuran, was heated to 160-170°, and then oxidized. In both cases, the amount of phenylmethylcarbinol in the mixture of isomeric phenylethyl alcohols obtained from the separate oxidations was 15-18%. In view of the formation of a mixture containing both triphenylethylboron isomers we investigated the possibility of converting the primary derivative $(C_6H_5CH_2CH_2)_3B$ to the secondary derivative $[C_6H_5CH(CH_3)]_3B$. Tri-(β-phenylethyl)boron was obtained by the scheme:

$$C_6H_5CH_2CH_2MgBr + BF_3 \cdot (C_2H_5)_2O \longrightarrow (C_6H_5CH_2CH_2)_3B$$

After heating at 160-170°, the tri-(β-phenylethyl)boron obtained in this manner was subjected to oxidation, and here we obtained a mixture of the isomeric phenylethyl alcohols, containing 12-14% phenylmethylcarbinol. From this it follows that the tri-(β-phenylethyl)boron was isomerized to some extent to tri-(α-phenylethyl)boron. It is obvious that under certain conditions both of these compounds are found in equilibrium with each other:

$$(C_6H_5CH_2CH_2)_3B \rightleftharpoons (C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}H)_3B$$

EXPERIMENTAL

Reaction of triisobutylboron with styrene. A mixture of 15 g of styrene and 10 g of triisobutylboron was heated at 150-170° until the evolution of isobutylene ceased. At the end the reaction temperature was raised to 180°. Then the reaction mixture was cooled, dissolved in 50 ml of ether, and with ice water cooling a solution of 10 g NaOH in 30 ml of water was added. Then 25 ml of 28% hydrogen peroxide solution was added gradually at 5-10°. On distillation we obtained 12.5 g (71% of theoretical) of a mixture of phenylethyl alcohols with b.p. 89-92° (7 mm). Five grams of this mixture was oxidized with chromium trioxide in acetic acid at room temperature. The oxidation products were steam-distilled. The distillate was extracted with ether. After removal of the ether, the residue was treated with an alcohol solution of 2,4-dinitrophenylhydrazine in the presence of sulfuric acid. We obtained 1.95 g of acetophenone 2,4-dinitrophenylhydrazone (this corresponds to a 16% content of phenylmethylcarbinol) with m. p. 229-232°. After recrystallization from acetic acid the dinitrophenylhydrazone had m. p. 236-237°. Found: C 55.85, 55.85; H 3.96, 3.96%. $C_{14}H_{12}O_4N_4$. Calculated: C 55.98; H 4.00%.

Reaction of diborane with styrene. Diborane, obtained by reacting sodium aluminum hydride with boron trifluoride etherate, was passed, with ice water cooling, into a solution of 20 g of styrene in 75 ml of tetrahydrofuran. The absorption of the diborane led to a rise in the temperature. The reaction mixture was divided into two parts; one part was oxidized with alkaline hydrogen peroxide, as described in the preceding experiment. We obtained 10.6 g (86% of theoretical) of a mixture of phenylethyl alcohols with b.p. 89-92° (7 mm). From 5 g of this mixture we obtained 2.1 g of acetophenone 2,4-dinitrophenylhydrazone, which corresponds to a 17% content of phenylmethylcarbinol. The tetrahydrofuran was distilled from the second portion, and the residue was heated at 160-170° for 2 hr. After dissolving in 50 ml of ether the material was oxidized with alkaline hydrogen peroxide. We obtained 8.4 g of mixed phenylethyl alcohols. From 5 g of this mixture we obtained 2.2 g of acetophenone 2,4-dinitrophenylhydrazone, which corresponds to an 18% content of phenylmethylcarbinol.

Reaction of β-phenylethylmagnesium bromide with boron trifluoride. To 5 g of magnesium turnings and 80 ml of ether was gradually added 37 g of β-phenylethyl bromide, prepared from β-phenylethyl alcohol* and phosphorus tribromide. To the obtained Grignard compound, with stirring and cooling, was gradually added 7.5 g of boron trifluoride etherate in 20 ml of ether, in a nitrogen atmosphere. The reaction mixture was heated under reflux for 30 min, cooled, and then treated with 200 ml of oxygen-free water. The ether layer was separated, washed with water, and dried over magnesium sulfate in a nitrogen atmosphere. After distilling off the ether and removal of the volatile products in vacuo, the residue was heated at 160-170° for 2 hr. On oxidation, as described in the preceding experiments, we obtained 11.8 g (61% of theoretical) of mixed phenylethyl alcohols with b.p. 90-92° (7 mm). From 5 g of this mixture we obtained 1.7 g of acetophenone 2,4-dinitrophenylhydrazone, which corresponds to a 13% content of phenylmethylcarbinol.

The quantitative determination of the composition of the mixture was done in the Optical Laboratory by N. A. Chumaevskii, for which the authors express their deep gratitude.

SUMMARY

1. The reaction of triisobutylboron and of diborane with styrene both yield a mixture of tri-(phenylethyl)borons, containing the boron atom in both the α- and β-positions to the phenyl group.

2. Tri-(β-phenylethyl)boron when heated is partially isomerized to tri-(α-phenylethyl)boron.

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*The oxidation of β-phenylethyl alcohol with chromium trioxide and subsequent treatment with 2,4-dinitrophenylhydrazine did not give acetophenone 2,4-dinitrophenylhydrazone, but instead a small amount of benzaldehyde 2,4-dinitrophenylhydrazone was isolated.

SYNTHESIS AND PROPERTIES OF B-TRI-n-BUTYLMERCAPTOBORAZOLES

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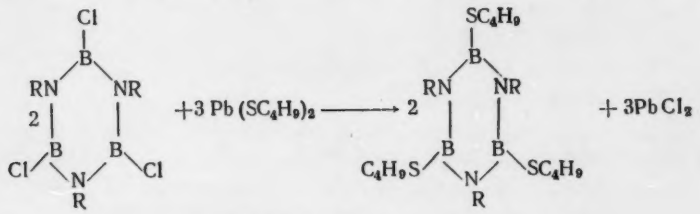
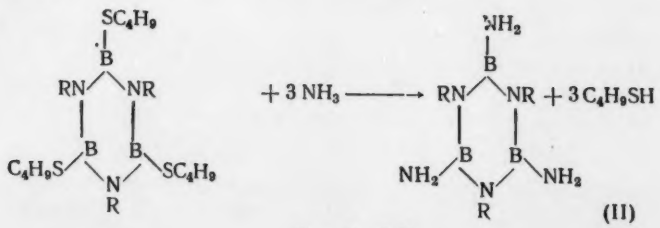
In connection with the high reactivity shown by the esters of thioboronic acids [1-3] it seemed of interest to synthesize the B-alkylmercapto derivatives of borazole and make a study of their chemical properties. By analogy with the behavior of organoboron halides toward mercaptans [3], it might be expected that the alkylmercapto derivatives of borazole could be obtained by heating the B-trichloro derivatives of borazole and its homologs with mercaptans. However, this method proved to be unsuitable for the synthesis of alkylmercapto derivatives in the borazole series. Replacement of the chlorine atoms in the B-trichloro derivatives of borazole could be accomplished by heating the latter compounds with lead mercaptides in benzene medium.

The reaction of lead n-butylmercaptide with B-trichloroborazole, B-trichloro-N-trimethylborazole or B-trichloro-N-triethylborazole gave us respectively B-tri-n-butylmercaptoborazole (I) (R = H), B-tri-n-butylmercapto-N-trimethylborazole (I)(R = CH_3), and B-tri-n-butylmercapto-N-triethylborazole (I) (R = C_2H_5).



R = H, CH_3, C_2H_5 (I)

Like the esters of thioboronic acids, the obtained B-n-butylmercaptoborazoles exhibit a high reactivity. When reacted with alcohols they exchange the n-butylmercapto groups for alkoxyl radicals, being converted to B-trialkoxyborazoles. Thus, the reaction of methanol with B-tri-n-butylmercaptoborazole yields B-trimethoxyborazole. The B-tri-n-butylmercaptoborazoles react in the cold with both primary and secondary amines, forming N-substituted derivatives of B-triaminoborazole and B-triamino-N-trialkylborazoles. The reaction of dimethylamine or aniline with B-tri-n-butylmercaptoborazole gave respectively B-tri-(dimethylamino)borazole and B-triphenylaminoborazole, while the reaction of B-tri-n-butylmercapto-N-triethylborazole with aniline gave B-triphenylamino-N-triethylborazole. A partial replacement of the alkylmercapto groups by N-alkylamino radicals could not be accomplished. The reaction of 2 moles of aniline with 1 mole of B-tri-n-butylmercaptoborazole gave B-triphenylaminoborazole, while a portion of the starting borazole derivative failed to react. The passage of ammonia into a benzene solution of B-tri-n-butylmercaptoborazole or B-tri-n-butylmercapto-N-triethylborazole led to replacement of the alkylmercapto groups by amino groups with the respective formation of B-triaminoborazole (II)(R = H) and B-triamino-N-triethylborazole (II) (R = C_2H_5).



R = H, C_2H_5 (II)

EXPERIMENTAL

All of the operations were conducted in a nitrogen atmosphere.

B-Tri-n-burylmercaptoborazole (I) (R = H). To a solution of 6.0 g (0.033 mole) of B-trichloroborazole [4] in 70 ml of dry benzene was added, with stirring, 19.0 g (0.049 mole) of lead n-butylmercaptide. Then the reaction mixture was refluxed for 2 hr. The obtained precipitate of lead chloride was filtered and washed with benzene. After distilling off the benzene and vacuum-distillation of the residue we obtained 10.6 g (91%) of compound (I) as a colorless liquid with b. p. 175-180° (0.3 mm), which crystallized on cooling; b. p. 15-18°; d^{20}_4 1.0356; $n^{20}D$ 1.5348; found MR 103.23; calculated MR 105.42. Found: C 42.16, 42.41; H 8.62, 8.71; B 9.2, 9.0%. $C_{12}H_{30}B_3N_3S_3$. Calculated: C 41.77; H 8.76; B 9.4%.

B-Tri-n-butylmercapto-N-trimethylborazole (I) (R = CH_3). In an analogous manner, from 4.4 g (0.019 mole) of B-trichloro-N-trimethylborazole [5] and 11.5 g (0.3 mole) of lead n-butylmercaptide we obtained 5.2 g (70%) of B-tri-n-butylmercapto-N-trimethylborazole with b. p. 180-185° (0.05 mm); d^{20}_4 1.0290; $n^{20}D$ 1.5360; found MR 117.50; calculated MR 119.85. Found: C 47.17, 47.13; H 9.34, 9.53; B 8.05, 8.41%. $C_{15}H_{36}B_3N_3S_3$. Calculated: C 46.54; H 9.37; B 8.38%.

B-Tri-n-burylmercapto-N-triethylborazole (I) (R = C_2H_5). From 15.6 g (0.058 mole) of B-trichloro-N-triethylborazole [5] and 33.6 g (0.087 mole) of lead n-butylmercaptide we obtained 18.7 g (76%) of B-tri-n-butylmercapto-N-triethylborazole with b. p. 130-135° (0.1 mm); d^{20}_4 1.0060; $n^{20}D$ 1.5228; found MR 132.25; calculated MR 133.79. Found: C 49.88, 49.58; H 9.52, 9.30; B 7.77, 7.75%. $C_{18}H_{42}B_3N_3S_3$. Calculated: C 50.37; H 9.86; B 7.60%. All of the obtained B-trialkylmercaptoborazoles are readily soluble in benzene, isopentane, and ether.

B-Trimethoxyborazole. To 6.20 g (0.018 mole) of B-tri-n-butylmercaptoborazole (I) (R = H) in 25 ml of benzene was added in 15 min, with stirring, 1.7 g (0.054 mole) of dry methyl alcohol. After stirring for 1 hr, the solvent and liberated n-butyl mercaptan were vacuum-distilled. The residue was sublimed at 60° (2 mm). We obtained 1.5 g (50%) of B-trimethoxyborazole with m. p. 102-105° (in a sealed capillary). From the literature [6]: m. p. 110-112°.

B-Tri-(dimethylamino)borazole. In an analogous manner, from 2.2 g (0.06 mole) of B-tri-n-butylmercaptoborazole (I) (R = H) in 10 ml of benzene and 0.8 g (0.02 mole) of dimethylamine we obtained 1.3 g (97%) of B-tri-(dimethylamino)borazole, which was purified by sublimation at 95° (2 mm). The compound was obtained as colorless crystals with m. p. 108-110° (in a sealed capillary). From the literature [4]: m. p. 112-113°.

B-Triphenylaminoborazole. To a solution of 3.5 g (0.01 mole) of B-tri-n-butylmercaptoborazole (I) (R = H) in 15 ml of benzene was added, with stirring, 3.0 g (0.03 mole) of aniline in 5 ml of benzene. A slight heating up of the reaction mass was observed, as well as the deposition of a precipitate after an hour. The precipitate was filtered; the filtrate was evaporated in vacuo to dryness. The combined residue and filtered precipitate (3.4 g) was recrystallized from benzene. We obtained 2.5 g (70%) of B-triphenylaminoborazole with m. p. 204-206° (in a sealed capillary). Found: C 60.71, 60.59; H 6.06, 6.25; B 9.03, 9.03%. $C_{18}H_{21}B_3N_6$. Calculated: C 61.0; H 6.12; B 9.16%. B-Triphenylaminoborazole is a colorless crystalline compound, difficultly soluble in boiling benzene, and insoluble in isopentane and ether.

B-Triphenylamino-N-triethylborazole. In an analogous manner, from 3.3 g (0.008 mole) of B-tri-n-butylmercapto-N-triethylborazole (I) (R = C_2H_5) in 15 ml of benzene and 2.1 g of aniline (0.022 mole) in 5 ml of benzene we obtained 1.83 g (55.3%) of B-triphenylamino-N-triethylborazole with b. p. 210-215° (0.1 mm), which crystallized on cooling; m. p. 48-50° (in a sealed capillary). Found: C 64.80, 64.89; H 7.38, 7.68; B 7.51, 7.68%. $C_{24}H_{33}B_3N_6$. Calculated: C 65.80; H 7.59; B 7.41%.

B-Triaminoborazole (II) (R = H). With stirring, dry ammonia was passed for 15 min into a solution containing 6.9 g (0.02 mole) of B-tri-n-butylmercaptoborazole (I) (R = H) in 50 ml of benzene. Here we observed a warming up of the reaction mixture and the deposition of a colorless crystalline precipitate, which was filtered, washed with isopentane, and dried in vacuo. We obtained 2.05 g (80%) of B-triaminoborazole, which proved to be insoluble in benzene, isopentane and ether, does not melt up to 250°, and decomposes with the evolution of ammonia. Found: C B 25.87, 26.1%. $B_3N_6H_9$. Calculated: B 25.80%.

B-Triamino-N-triethylborazole (II) (R = C_2H_5). A warming up of the reaction mass was observed when dry ammonia was passed into a solution of 4.7 g (0.01 mole) of B-tri-n-butylmercapto-N-triethylborazole (I) (R = C_2H_5).

The solvent and n-butyl mercaptan were removed by distillation. The residue (2.7 g) was vacuum-distilled. We obtained 1.2 g (60%) of substance with b. p. 90-91° (0.1 mm); m. p. 33-35° (in a sealed capillary). Found: C 35.49; H 10.33; B 15.34%. $C_6H_{21}B_3N_6$. Calculated: C 34.36; H 10.09; B 15.48%. B-Triamino-N-triethylborazole is readily soluble in benzene, ether, and isopentane.

SUMMARY

Some B-tri-n-butylmercapto derivatives of borazole were synthesized by the reaction of lead n-butylmercaptide with B-trichloroborazole and its homologs. A study was made of the reactions of the synthesized borazole derivatives with methyl alcohol, amines, and ammonia.

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STUDY OF THE STEPWISE DEHYDRATION OF 1,6-HEXANEDIOL ON TRICALCIUM PHOSPHATE CATALYST

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The catalytic dehydration of C_4 and higher ω-glycols proceeds in a stepwise manner. Polymethylene oxide and the isomeric unsaturated alcohol are formed in the first stage of the process. The second molecule of water is cleaved with greater difficulty. As a result, the end reaction product, the diolefin, can be obtained by two procedures: by the dehydration of either the oxide or the unsaturated alcohol. As we had previously shown, in the presence of phosphate catalyst the formation of butadiene from 1,4-butanediol proceeds mainly through the butenol [1], while the formation of pentadienes from 1,5-pentanediol takes place through both the pentenol and tetrahydropyran [2]. The cleavage of water from 1,6-hexanediol using concd. sulfuric acid gave α-methyltetrahydropyran and α-ethyltetrahydrofuran [3], while using 57% sulfuric acid gave hexamethylene oxide [4]. The dehydration of 1,6-hexanediol on solid catalysts has not been studied.

EXPERIMENTAL

In the present paper a study was made of the stepwise dehydration of 1,6-hexanediol under flow conditions using a phosphate catalyst [5]. The catalyst volume was 25 ml and the granule size was 2 × 3 mm. At the end of experiment the catalyst was regenerated in a stream of air at 400-450°. The hexanediol had b. p. 127° (5 mm) and m. p. 40°. In each experiment we passed 20 ml of the glycol at a rate of 17.5 ml/hr. Study revealed that even at the lower temperatures (320-330°), where the reaction only began to proceed, a simultaneous formation of both the partial and complete dehydration products of the diol occurred. Consequently, after drying over potassium carbonate, the obtained catalyzates were fractionally distilled into fractions containing diolefin (55-90°), hexamethylene oxide (100-130°), and hexenol (140-160°). Unreacted diol was recovered from the residue by vacuum-distillation. Examples of investigating the composition of these fractions are given below.

The fractional distillation of 14.5 g of the diolefin fraction through a column with an efficiency of 15 theoretical plates gave four fractions, the properties of which are given below: I) 3.1 g; b. p. 61-64°; d^{20}_4 0.7031; $n^{20}D$ 1.4110; II) 1.8 g; b. p. 66-70°; $n^{20}D$ 1.4185; III) 1.6 g; b. p. 74-78°; d^{20}_4 0.7523; $n^{20}D$ 1.4398; IV) 7.3 g; b. p. 80-81.5°; d^{20}_4 0.7638; $n^{20}D$ 1.4481. Approximately 2 moles of hydrogen was absorbed when a known amount of each of these fractions was hydrogenated. The Raman spectra of fractions I and II exhibited frequencies at 1642 and 1679 cm^{-1}, characteristic for the isolated double bonds in 1,5-hexadiene and 1,4-hexadiene [6]. The spectrum of fraction III exhibited the frequencies [1658 (10), 1442 (5 wide), 1328 (0), 1279 (6), 1244 (4), 1180 (5 very wide), 1110 (0), 1068 (1), 1020 (1), 900 (1) and 846 (0)] of the spectrum of 1,3-hexadiene [6]. The spectrum of fraction IV exhibited the frequencies [1628 (10), 1453 (3), 1379 (4), 1303 (5), 1280 (1), 1263 (1), 1240 (3), 434 (4)] of 2,4-hexadiene [6].

From 25.2 g of the fraction with b. p. 100-130° we isolated by fractional distillation through the column the following fractions: Ia) 1.0 g; b. p. 95-103°; $n^{20}D$ 1.4258; IIa) 1.2 g; b. p. 104-110°; $n^{20}D$ 1.4178; IIIa) 5.9 g; b. p. 113-115°; d^{20}_4 0.8594; $n^{20}D$ 1.4200; IVa) 14.1 g, b. p. 119-120°; d^{20}_4 0.9037; $n^{20}D$ 1.4394. The last fraction exhibits the properties of the recently described hexamethylene oxide [7]; b. p. 119-120°; d^{20}_4 0.9036; $n^{20}D$ 1.4393. Found: C 71.59; H 12.00%. $C_6H_{12}O$. Calculated: C 72.00. H 12%. Found MR 29.19; calculated MR 29.31; its infrared spectrum concides completely with the spectrum of hexamethylene oxide [7]. Consequently, the main component of the 100-130° catalyzate fraction is hexamethylene oxide. This fraction also contained a carbonyl compound as impurity, about 4-6% when calculated as caproaldehyde.

Together with hexamethylene oxide, we also obtained a small amount of α-methyltetrahydropyran and α-ethyltetrahydrofuran; the method of gas-liquid chromatography was used to determine them. The curves for the

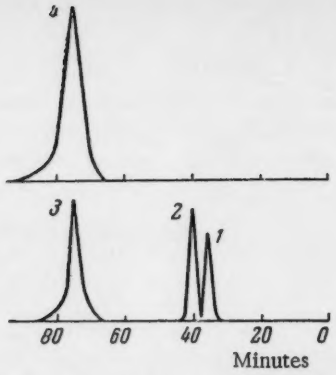


Fig. 1. Chromatograms of a mixture of α-methyltetrahydropyran (1), α-ethyltetrahydrofuran (2) and hexamethylene oxide (3), and of fraction 4a (4).

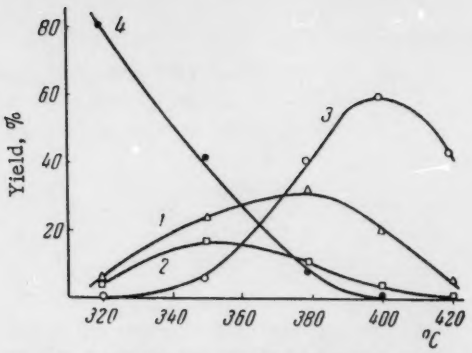


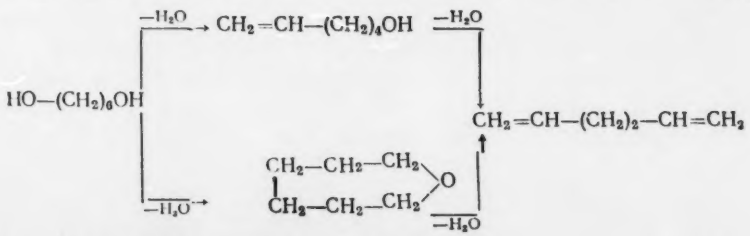
Fig. 2. Dehydration of 1,6-hexanediol; 2) hexamethylene oxide; 2) hexenol; 3) hexadiene; 4) unreacted diol.

separation of a mixture of synthetic α-methyltetrahydropyran, α-ethyltetrahydrofuran and hexamethylene oxide and the chromatogram of fraction IVa (support – tricresyl phosphate, temperature – 90°, length of column – 2 mm) are shown in Fig. 1. From Fig. 1, it can be seen that the mixture of the three oxides is easily separated. We used this method to determine in fraction Ia: 48% α-methyltetrahydropyran and 11% α-ethyltetrahydrofuran, and in fraction IIa: 42% α-methyltetrahydropyran and 31% α-ethyltetrahydrofuran. Fraction IIIa consisted mainly (75%) of hexamethylene oxide, while fraction IVa was pure hexamethylene oxide. From the catalyzate fraction with b. p. 140-160° we isolated a product (74 wt. %) with b. p. 155-158° (755 mm) and 43-46° (4 mm); d^{20}_4 0.8418; $n^{20}D$ 1.4375. The Raman spectrum method was used to show the presence of double bonds in this fraction, mainly in the α-position (1642 cm^{-1}), and partially in another position (1678 cm^{-1}). The amount of hexenol, determined by the bromine number method and by acetylation in pyridine, was respectively 100 and 94%. The properties of the isolated product lie close to the properties of 5-hexen-1-ol: b. p. 74° (25 mm); $d^{23.5}_4$ 0.834; $n^{23.5}D$ 1.4341 [8]. Apparently, both α-methyltetrahydropyran and α-ethyltetrahydrofuran are isomerization products of hexamethylene oxide, while the different hexadienes are apparently isomerization products of 1,5-hexadiene.

In order to establish the stage mechanism of the process we investigated the influence of temperature on the reaction course.

From Fig. 2, it can be seen that the maximum yield of the hexenol, 17%, is obtained at 350°, that of hexamethylene oxide, 32%, is obtained at 380°, and that of the hexadienes, 60%, at 400°. At 420° the total yield of these compounds drops due to the incipient decomposition. An intense formation of the diolefin at temperatures above 350°, with a simultaneous increase in the yield of hexamethylene oxide and a decrease in the yield of the hexenol, indicates that the diolefin is formed mainly from the hexenol, which, apparently, is less stable than the oxide. Actually, when passed over the catalyst at 400°, the extent to which the hexenol was converted to the hexadiene was 75-80%, while in the case of hexamethylene oxide the conversion to the hexadiene was only 18%. The oxide could not be detected in the dehydration products of the alcohol, and consequently hexamethylene oxide was not formed in the isomerization of the hexenol.

The obtained data make it possible to conclude that the dehydration of 1,6-hexanediol over phosphate catalyst to the hexadiene:



takes place predominantly through the stage of forming the hexenol.

The authors wish to thank V. V. An and B. L. Lebedev for performing the chromatographic analyses.

SUMMARY

1. The dehydration of 1,6-hexanediol on tricalcium phosphate catalyst results in the simultaneous formation of both the partial (hexenol, hexamethylene oxide) and complete (hexadiene) dehydration products of the glycol. The latter (hexadiene) is obtained mainly through the intermediate formation of the hexenol, which is less stable than the oxide.

2. Isomerization of the formed oxide and migration of the double bonds in the diolefin accompany the main process.

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THE REACTION OF β-NITRO ALCOHOLS WITH ETHOXYACETYLENE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 2, pp. 375-376, February, 1961
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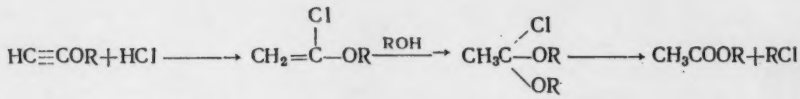
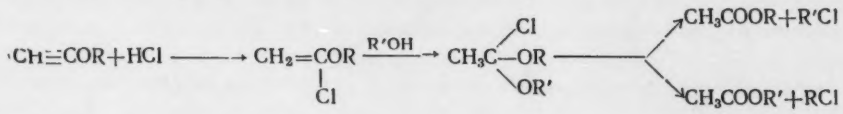
Favorskii and Shchukina [1] studied the reaction of alcohols with alkoxyacetylenes in the presence of equivalent amounts of hydrogen chloride; they showed that the first stage of the reaction is the addition of hydrogen chloride to the triple bond with the formation of α-chlorovinyl ethers, and they proposed the following reaction scheme:

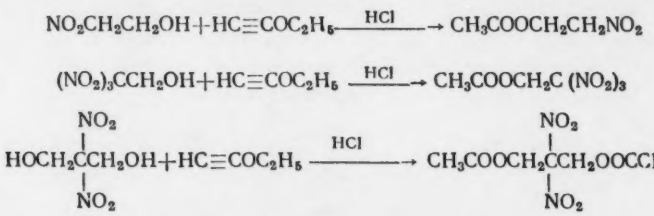


However, since Favorskii and Shchukina ran the reaction for cases where the radicals in both the alkoxyacetylene and the alcohol were the same, the mechanism of the reaction was not sufficiently clear. Actually, in the case of different radicals it is possible to postulate two different directions of the reaction course:



In 1953 Rix and Arens [2] described the reaction of α-chlorovinyl ethyl ether, obtained by the addition of hydrogen chloride to ethoxyacetylene, with various alcohols and showed that the reaction actually goes into two directions. On the basis of a series of experiments the indicated authors come to the conclusion that the reaction goes preferentially in the direction of forming the more reactive chloride. Thus, when R = C_2H_5 and R' = $(C_6H_5)_3C$, the main reaction products are $(C_6H_5)_3CCl$ and $CH_3COOC_2H_5$; also, a good yield of benzyl chloride (together with the formation of $CH_3COOC_2H_5$ and $CH_3COOCH_2C_6H_5$) is obtained when R = C_2H_5 and R' = $C_6H_5CH_2$. At the same time the acetates were obtained from phenol and β-naphthol, but the corresponding chlorides were not isolated.

We ran the reaction of ethoxyacetylene with a number of β-nitro alcohols. The reaction of ethoxyacetylene with nitroethanol, trinitroethanol and 2,2-dinitropropanediol in the presence of hydrogen chloride led to the formation of the acetates, and in not a single case were we able to isolate the corresponding chlorides.



For purposes of identification, the acetates of 2-nitroethanol, 2,2,2-trinitroethanol and 2,2-dinitropropanediol were also synthesized by the esterification of the nitro alcohols with acetic anhydride in the presence of concd. sulfuric acid. In the light of the conclusions made by Rix and Arens [2], the obtained results give reason to believe that the halogen in β-nitrohaloalkanes is less labile than in the corresponding "pure" aliphatic halides. For example, the chlorine in chloroethane is probably more labile than the chlorine in β-nitrochloroethane and, to an even greater degree, than the chlorine in β,β,β-trinitrochloroethane. This is in complete accord with the data of Knunyants [3],

who established that when the halogen is found in the β-position to electron-acceptor groups it is less labile than when not exposed to such influence (for example, the bromine atom in F_3CCH_2Br is hydrolyzed with very great difficulty).

EXPERIMENTAL

Into a four-necked flask, fitted with a glycerin-seal mechanical stirrer, reflux condenser, dropping funnel and thermometer, were charged the appropriate alcohol and absolute ether, the latter containing dry hydrogen chloride (1 g of HCl per 10 ml of ether); with stirring and ice-cooling, a solution of ethoxyacetylene in absolute ether was added from the dropping funnel at such a rate that the temperature of the mixture did not exceed 0-5°. After exothermic reaction had ceased, the mixture was heated under reflux with stirring, then cooled, neutralized with solid $NaHCO_3$, and filtered. The ether solution was evaporated, and the residue was repeatedly washed with water, after which it was dissolved in ether, dried over magnesium sulfate, and fractionally distilled.

Nitroethanol. A mixture of 36 ml of (ether + HCl), 9.1 g of nitroethanol and a solution of 7 g of ethoxyacetylene in 25 ml of ether were refluxed for 4 hr. We obtained 4.9 g (37% of theory) of the acetate of the nitroethyl alcohol with b. p. 91° (10 mm); 67° (2 mm); $n^{20}D$ 1.4361; d^{20}_4 1.2227. When 2-nitroethanol was reacted with acetic anhydride the acetate had b. p. 70-72° (4 mm); $n^{20}D$ 1.4363; d^{20}_4 1.2220. Found: C 38.71, 38.93; H 5.58, 5.72; N 11.11, 11.25%. $C_4H_7NO_4$. Calculated: C 39.02; H 5.69; N 11.38%.

Trinitroethanol. In a similar manner, from 18 ml of (ether + HCl), 9 g of trinitroethanol and a solution of 3.5 g of ethoxyacetylene in 15 ml of ether we obtained 7.2 g (64% of theory) of the acetate of the trinitroethyl alcohol; 78-82° (3 mm); $n^{20}D$ 1.4511; d^{20}_4 1.4757. The esterification of 2,2,2-trinitroethanol with acetic anhydride gave the acetate with b. p. 90° (4 mm); $n^{20}D$ 1.4528; d^{20}_4 1.4743. Literature data [4]: b. p. 118° (4 mm); $n^{20}D$ 1.4478.

2,2-Dinitropropanediol. A mixture of 18 ml of (ether + HCl), 8.4 g of 2,2-dinitropropanediol (cooling is necessary when the diol is added to the ether + HCl, since the mixture heats up) and a solution of 3.5 g of ethoxyacetylene in 10 ml of ether was refluxed for 7 hr. After distilling off the ether, the residue crystallized partially. The liquid portion was separated and fractionally distilled. We obtained 1.8 g (19% of theory) of the diacetate of 2,2-dinitropropanediol with b. p. 130-131° (3.5 mm); $n^{20}D$ 1.4518; d^{20}_4 1.3448. The diacetate of 2,2-dinitropropanediol was also obtained by reacting the diol with acetic anhydride; b. p. 132.5° (4 mm); $n^{20}D$ 1.4528; d^{20}_4 1.3437. Found: C 33.47, 33.58; H 3.96, 4.11; N 11.01, 11.17%. $C_7H_{10}N_2O_8$. Calculated: C 33.60; H 4.00; N 11.20%.

SUMMARY

1. Ethoxyacetylene was reacted with 2-nitroethanol, 2,2,2-trinitroethanol and 2,2-dinitropropanediol in the presence of hydrogen chloride and the corresponding acetates were obtained.

2. The theory was expressed that the chlorine atom in β-nitrochloroalkanes in less labile than the chlorine atom in the corresponding unsubstituted aliphatic chloroparaffins.

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LETTERS TO THE EDITOR

A NEW REACTION OF HALOLACTONES

Yu. A. Arbuzov, M. N. Kolosov, Yu. A. Ovchinnikov,

and M. M. Shemyakin

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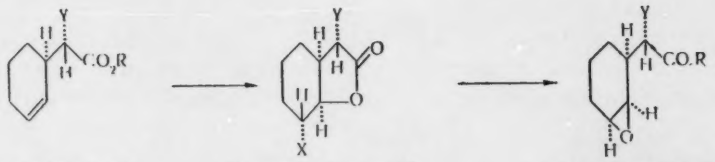
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 2, p. 377, February, 1961

Original article submitted November 15, 1960

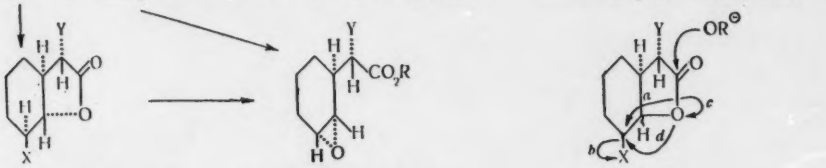
When acids (I) were reacted with either I_2 or Br_2 in sodium carbonate solution we obtained the halolactones (III) and the halohydroxy acids, which were then cyclized to the haloactones (V) (their structure was established from the infrared spectra and by dehalogenation to previously described substances [1]). In attempting to saponify (III) and (V) with 1 equiv. of KOH in MeOH, EtOH or $PhCH_2OH$ (20°, 4 hr) we discovered a peculiar reaction, leading to a nearly quantitative yield of epoxy esters (IV) and (VI); compounds (VI) were also obtained from ethers (II) by oxidation with $PhCO_3H$.



(I)a: R=H, Y=H (b.p.$_{10}$ 132°)
(I)b: R=H, Y=NHAc (m.p. 179°)
(I)c: R=H, Y=NHCHO (m.p. 163°)
(II)a: R=Et, Y=H (b.p.$_{10}$ 86°)
(II)b: R=Me, Y=NHAc (m.p. 103°)
(II)c: R=Me, Y=NHCHO (m.p. 140°)

(III)a: X=I, Y=H (m.p. 66°)
(III)b: X=Br, Y=H (m.p. 59°)
(III)c: X=I, Y=NHAc (m.p. 164°)
(III)d: X=Br, Y=NHAc (m.p. 179°)
(III)e: X=I, Y=NHCHO (m.p. 173°)
(III)f: X=Br, Y=NHCHO (m.p. 180°)

(IV)a. R=Me, Y=H (b.p.$_1$ 95°)
(IV)b: R=Me, Y=NHAc (m.p. 101°)
(IV)c: R=Me, Y=NHCHO (m.p. 61°)
(IV)d: R=Et, Y=H (b.p.$_2$ 90°)
(IV)e: R=Et, Y=NHAc (m.p. 96°)
(IV)f: R=CH_2Ph, Y=NHAc (m.p. 107°)



(V)a: X=Br, Y=NHAc (m.p. 173°)
(V)b: X=Br, Y=NHCHO (m.p. 150°)

(VI)a: R=Et, Y=H (b.p.$_1$ 90°)
(VI)b: R=Me, Y=NHAc (m.p. 100°)
(VI)c: R=Me, Y=NHCHO (m.p. 55°)

(VII)

It is evident that shifts, shown in formula (VII): synchronous (a and b) or consecutive (c, then d and b), occur when the carbonyl is attacked by RO^- anion. This reaction also lies at the base of other transformations of the δ-halo-γ-lactones, for example, their alkaline hydrolysis to δ-hydroxy-γ-lactones [2].

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SYNTHESIS OF SIMPLE ENOLATES OF ALUMINUM

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We discovered a method for obtaining the previously unknown simple enolates of aluminum, which consists in reacting dialkylaluminum hydrides with trialkylvinyloxysilanes. With this procedure we obtained diisobutylvinyloxyaluminum and diisobutylpropenyloxyaluminum in accordance with the scheme:

$$i\text{-}Bu_2AlH + (C_2H_5)_3SiOCH{=}CH_2 \longrightarrow i\text{-}Bu_2AlOCH{=}CH_2 + (C_2H_5)_3SiH$$

$$i\text{-}Bu_2AlH + (C_2H_5)_3SiOCH{=}CH{-}CH_3 \longrightarrow i\text{-}Bu_2AlOCH{=}CH{-}CH_3 + (C_2H_5)_3SiH$$

With stirring, 8 g of triethylvinyloxysilane was added to 7.2 g of the hydride at such a rate that the temperature did not rise above 40°. After heating at 50-55° for 1 hr the reaction mixture was vacuum-distilled. We obtained 4.8 g of triethylsilane with b. p. 106-107° and 6.3 g of diisobutylvinyloxyaluminum with b. p. 99-100° (1 mm). Found: C 65.37, 65.46; H 11.70, 11.68; Al 14.70, 14.75%. $C_{10}H_{21}AlO$. Calculated: C 65.20; H 11.48; Al 14.64%.

On hydrolysis we obtained isobutane and acetaldehyde, the latter being characterized as the 2,4-dinitrophenylhydrazone, m. p. 165-166°. Diisobutylpropenylaluminum has b. p. 110-111° (1 mm). Found: C 66.78, 66.81; H 11.92, 12.03; Al 14.17, 14.27%. $C_{11}H_{23}AlO$. Calculated: C 66.66; H 12.12; Al 13.63%.

The obtained compounds have an enolate structure, since their Raman spectra show the presence of a double bond and do not contain the frequencies characteristic for a carbonyl group.

THE IONIZATION OF TERT-ALKYL TRIFLUOROACETATES IN ANHYDROUS TRIFLUOROACETIC ACID

V. N. Setkina and D. N. Kursanov

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR
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We discovered that in tert-alkyl trifluoroacetates the hydrogen atoms are replaced with astonishing ease by deuterium when these esters are dissolved in anhydrous, deuterium-enriched trifluoroacetic acid. The isotopic equilibrium is established so rapidly that the rate constant of the hydrogen exchange cannot be measured under ordinary conditions.

For example, it proved that tert-butyl trifluoroacetate, isolated after 30 min from a solution of deuterated trifluoroacetic acid (molar ratio 1: 5), had undergone profound hydrogen exchange at room temperature. An even greater rate of hydrogen exchange is observed for 1-methylcyclohexyl-1-trifluoroacetate.

Apparently, the hydrogen exchange shown by alkyl trifluoroacetates under the indicated conditions is due to the ease of ionization of the alkyl-oxygen bond in these esters, in accordance with the scheme:

$$\text{tert.}\ R{-}O{-}\overset{\overset{O}{\|}}{C}{-}CF_3 \underset{Solv}{\rightleftarrows} [\text{tert.}\ \overset{\oplus}{R}]_{Solv}\,[\overset{\ominus}{O}COCF_3]_{Solv} \rightleftarrows$$

$(CF_3)COOD)$ deuterium exchange (CF_3COOD)

$$\rightleftarrows [\text{tert.}\ \overset{\oplus}{R}_D]_{Solv}\,[\overset{\ominus}{O}COCF_3]_{Solv}$$

The formation of stabilized tert-alkyl carbonium ions and trifluoromethyl acetate anion, and also the high solvating capacity of trifluoroacetic acid, should facilitate such ionization.

The detailed data will be reported later.

CHRONICLE

GENERAL MEETING OF THE CHEMICAL SCIENCES SECTIONS OF THE ACADEMY OF SCIENCES OF THE USSR, OCTOBER 27-28, 1960

Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 2, pp. 379-380, February, 1961

At the general meeting of the Sections, Academician N. N. Semenov, Secretary of the Sections, presented an introductory paper on the problems of drawing up a plan of the general perspectives for the development of the national economy in the USSR for the period through 1980 and made some suggestions on the development of chemical science.

N. N. Semenov characterized the importance of chemistry for the national economy of the country and named the more important directions of the development of chemical science. Dwelling individually on the theoretical problems of chemistry, he mentioned the importance of further development of the theory of chemical structure, the theory of valence and chemical forces, the theory of the mechanism of chemical reactions, the problem of bioorganic chemistry and, in particular, the study of substances that function as the base of living material, the problem of the broad new field of organic chemistry – the chemistry of heteroorganic compounds, and a number of others. N. N. Semenov discussed the need of a broad development of contemporary physical methods of study–mass–spectrometry, electronic paramagnetic resonance, nuclear resonance, electron microscopy, neutronography, etc., and also the use of modern computation techniques for performing all kinds of calculations.

Academician B. A. Kazanskii reported on the problem of the development of scientific studies in the field of heavy organic synthesis. He indicated, as one of the more important tasks, the selection of readily available, cheap raw materials for creating a large variety of organic products. Such raw materials would have independent importance for the national economy, as well as serving as starting substances for the preparation of polymeric materials. Academician B. A. Kazanskii reported on a number of studies, devoted to increasing the yields and resources of ethylene, propylene, butadiene, isoprene, ethylbenzene, naphthalene, acetic acid, glycerol, etc. A number of new monomers will be created for obtaining high-molecular compounds. Important consideration will be given to the development of methods for the separation of both gaseous and liquid hydrocarbon mixtures.

Academician M. I. Kabachnik reported on the problems associated with the development of fine organic synthesis, and he mentioned the importance of this problem for the public health and nutrition. He emphasized the importance of the tasks relating to the creation of the foundations of molecular biology and the development of the chemistry of medicinals, in particular, the synthesis and study of drugs for combating tuberculosis, malignant tumors, and other diseases. Noting the complexity of solving these problems, M. I. Kabachnik pointed out the need of a close collaboration between chemists, physiologists, clinical physicians, toxicologists, and other specialists. The great importance to the country of intensifying the development of chemical preparations for use in agriculture (insecticides, herbicides, repellents, etc.) was mentioned.

The physical chemistry problem in the field of new building and construction materials was reported on by Academician P. A. Rebinder, who mentioned the need of creating materials with given structural-mechanical properties for diverse purposes, including various synthetic materials. Pointing out the importance of physicochemical factors in technological processes of dispersion, the blending of highly dispersed particles, and their compression under variable temperature and mechanical conditions, P. A. Rebinder mentioned the need to develop a new scientific discipline, which he named physicochemical mechanics.

Corresponding Member I. P. Alimarin reported on the problems relating to the development of basic chemistry, the chemistry of fertilizers, chemistry, and metallurgy. He stated that research is in progress on the development of a large number of methods for the processing of raw materials, including low temperature methods, adsorption, the use of ultrasonics, etc. Improved methods should be created for the production of the rare elements and new methods should be developed for obtaining ultrapure substances. The production of various chemical reagents, including inorganic, organic and biochemical, should receive broad development.

Academician A. N. Frumkin spoke on the problems facing the electrochemists, including the creation of various fuel elements, the wide use of electrolysis in the chemical industry, the production of coatings by the electrodeposition of metals, the use of electrolysis in metallurgy, the creation of new types of heat-resistant coatings, etc. A. N. Frumkin also pointed out the vast importance to the government of the problem of combating the corrosion of metals and named the more important tasks in this field.

The reviewed problems were discussed in order by Academician A. A. Balandin, Prof. A. V. Kiselev, Prof. M. V. Vol'kenshtein, S. V. Chepigo, V. P. Markov, Academician I. V. Tananaev, Corresponding Member I. A. Kazarnovskii, Corresponding Member N. I. Nikitin, K. M. Gorbunova, and A. I. Mikhailov.

Scientific papers at the general meeting were presented by: Academician A. A. Balandin on the theme "Some Problems in the Utilization of Catalysis in Chemical Technology." The speaker briefly reviewed a number of investigations being conducted in his laboratory and representing the development of practically important catalytic processes: the production of butadiene and isoprene, the preparation of monomers for ion-exchange resins – divinylbenzene, vinylpyridine, vinylthiophene, etc., the preparation of polyhydric alcohols and phenols by the hydrogenation of wood and its components, the process of ore-contact gasification, representing the simultaneous cracking of heavy petroleum fractions and the reduction of ores for the purpose of obtaining unsaturated gases, aromatic and other raw materials for the chemical industry, and also nonferrous metals.

Prof. Ya. T. Eidus spoke on the catalytic hydropolymerization reactions of olefins and their hydrocondensation with carbon monoxide. The speaker was able to collect data that testified to the formation of intermediate active forms on the surface of the cobalt catalyst, which affected both the course and direction of reaction. In the opinion of the speaker, these forms are methylene, alkyl, and other hydrocarbon radicals. The author expressed the theory that the hydrocondensation of olefins with carbon monoxide and hydropolymerization under the influence of CO are based on polymerization processes, and not on condensation-dehydration processes, in the growth of the hydrocarbon chains. It was shown by the speaker that the active forms arise on the catalyst surface not only from the carbon monoxide and olefin during their incomplete hydrogenation, but also in the processes of the destructive hydrogenation of the olefins.

Corresponding Member Ya. I. Gerasimov reported on the thermodynamic properties of binary metallic alloys, and he discussed the changes in the enthalpy, entropy and isobaric potential when a solid alloy is formed on pure (solid or liquid) metals. The systems discussed by him included copper–nickel (E.M.F.), cobalt–chromium (vapor pressure), antimony–copper (E.M.F.), vanadium–manganese (vapor pressure), and also antimony–tellurium, bismuth–tellurium, and indium–antimony (E.M.F.). The obtained data helped in deciphering the character of the interaction of metals in the formation of phases of variable composition and furnished material for the thermodynamic characterization of certain substances with semiconductor properties.

Corresponding Member B. V. Deryagin (co-author S. S. Dukhin) spoke on the diffusion theory of electrokinetic phenomena and its application to the preparation of latex films and suspensions and to foam flotation. The objective of the speaker was to show that taking diffusion into account makes it possible to not only introduce changes in the classical theory, but also to greatly expand the field embraced by it, including in it some completely new phenomena. The authors derived formulas for the rate of diffusion-borne suspended particles and for the capillary osmosis rate (movement) of the solution through a porous barrier under the influence of a drop in the electrolyte concentration. The phenomenon of diffusion cataphoresis was applied to constructing a quantitative theory for obtaining latex films when molds, coated on the surface with a layer of the electrolyte, are dipped in the latex suspension. This theory made it possible to work out a technique that not only greatly improved the quality of the obtained film, but also made it possible to obtain films from latices that previously had been considered unsuitable for this purpose.

Prof. A. V. Kiselev presented a paper on the chemical modification of highly dispersed substances (fillers and adsorbents). He mentioned that developing a theory of adsorption on solid substances is hindered by the indefiniteness of their chemical and geometric structure. This makes it impossible to express the adsorption properties by values bearing the character of physicochemical constants. In connection with this, a regulated change in the chemical nature of the surface possesses both theoretical and practical importance. The speaker studied both the chemical and crystallochemical modification of carbon black, and also a highly dispersed silica–aerosil and silica gel. It was shown by A. V. Kiselev that modified fillers and reinforcing materials bond well with polymeric media, while modified silica gels can serve as good adsorbents in gas chromatography, combining the advantages of both gas-liquid and gas-adsorption chromatography. By chemical modification of the solid substance it is possible to change the adsorption properties of the system by a matter of tens and even hundreds of times.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. —Publisher.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) } Dokl(ady) AN SSSR }	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
		Life Sciences: Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
		Life Sciences: Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
		Life Sciences: Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
		Earth Sciences: Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
		Earth Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1-6	1957-1958
		Earth Sciences: Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1-6	1957-1958
		Mathematics: Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
		Physics: Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
		Physics: Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)				
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations		1 1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union		1 1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute		1 1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1 1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3 1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1 1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1 1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1 1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1 1958
	Metallurg	Metallurgist	Acta Metallurgica		1 1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1 1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1 1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6 1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1 1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1 1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1 1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1 1958
PTÉ	(see Pribory i tekhn. éks.)				
	Problemy Severa	Problems of the North	National Research Council of Canada		
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1 1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1 1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1 1959
	Stal'	Stal (In English)	Iron and Steel Institute		1 1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1 1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4 1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1 1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1 1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1 1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1 1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1 1960
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UKh)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd		48 1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.		4 1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*		1 1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*		1 1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*		1 1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1 1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1 1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i teoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1 1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7 1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1 1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1 1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1 1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1 1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1 1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1 1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1 1958

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.